

# Philips Technical Review

DEALING WITH TECHNICAL PROBLEMS  
RELATING TO THE PRODUCTS, PROCESSES AND INVESTIGATIONS OF  
THE PHILIPS INDUSTRIES

EDITED BY THE RESEARCH LABORATORY OF N.V. PHILIPS' GLOEILAMPENFABRIEKEN, EINDHOVEN, NETHERLANDS

## FLUOROGRAPHY WITH THE AID OF A MIRROR SYSTEM

by W. HONDIUS BOLDINGH.

778.33: 771.313.26: 616.24-073.75

*From the point of view of the universality of the applied sciences the instrumentarium of the roentgenologist has long been one of the most interesting. Its development is related just as much to physics and mechanics as to biology, and there are also quite a number of economic considerations to be taken into account. In one of the most recent roentgenological methods, that of fluorography, also optics play one of the main parts. The application of the well-known Schmidt optical system in this field may well prove to bring about in the future a great change in the practice of X-ray diagnostics.*

### Introduction

Nowadays there are mainly three methods employed in X-ray diagnostics: fluoroscopy (screening), contact photography and fluorography. In screening, an X-ray image is formed on a fluorescent screen viewed by the physician direct. In contact photography a cassette containing a photographic film takes the place of the screen. In fluorography, with the aid of a camera set up at a distance from the patient, a reduced picture is made of the X-ray image visible on a fluorescent screen.

The principle of fluorography is not much younger than the other two methods, but it is only in the last fifteen years that it has been brought to development. Its field of application (for the present) is mainly mass chest survey in the fight against tuberculosis. It has the characteristic advantage of photography that the image is recorded, whilst with the small size of the recorded picture the heavy expense and the other drawbacks of contact photography are avoided. It is no exaggeration to say that it is this method of fluorography that has made periodical chest examination of large groups of the population a practical possibility.

In the development of the apparatus for fluorography there were two technical problems to solve: how to create the conditions for obtaining the best possible picture quality with the reduced photographs, and how to simplify the operation of the

apparatus as far as possible (considering that it may also have to be mobile).

These two problems have already been dealt with at some length in earlier publications in this journal <sup>1)</sup> <sup>2)</sup>. In particular a description has been given of a mobile installation for fluorography which was developed during World War II by the North American Philips Co. <sup>2)</sup> and attracted considerable attention. The working of this installation had been made so highly automatic that a continuous flow of 200 people per hour could be dealt with quite comfortably. Compared with this installation, the new apparatus for mass chest survey which have subsequently been developed by Philips show no essential changes as regards their operation and the technicalities connected therewith. But as regards the other problem mentioned — the conditions for an optimum picture quality — there has indeed been an important new development. This development, begun some ten years back, has led to the replacement of the previously used camera with lens system (a Fairchild camera with a Kodak Fluoro Ektar objective) by a camera with a mirror system having a much higher light-gathering power.

<sup>1)</sup> A. Bouwers and G. C. E. Burger, X-ray photography with the camera, Philips Techn. Rev. 5, 258-263, 1940.

<sup>2)</sup> H. J. Di Giovanni, W. Kes and K. Lowitzsch, A transportable X-ray apparatus for mass chest survey, Philips Techn. Rev. 10, 105-113, 1948.



Without entering into a renewed discussion of the problem of picture quality in fluorography it will be clear that, with a given X-ray intensity, the higher the light-gathering power of the camera the better will be the quality of the picture. It is then possible to use less sensitive fluorescent screens and/or films, which as a rule are finer-grained and thus able to give a sharper image; or else the exposure time can be made shorter, thereby reducing the kinetic blurring caused by the movement of the object (heart, blood vessels and lungs). Furthermore there is the advantage that the examinee receives a smaller dose of X-rays. The superiority of the mirror camera that has now been developed, as compared with the lens camera, is therefore most directly apparent in the exposure time required: whereas with the lens camera this was 0.1 to 0.5 sec, depending upon the thickness of the patient, now, other things being equal, 0.04 to 0.20 sec suffices.

This higher light-gathering power of the mirror camera can also be turned to advantage in quite a different way, namely by reducing the X-ray intensity required for the fluorographs. Accepting the same kinetic blurring as before, one can then manage with a much smaller and less expensive apparatus for generating the X-rays, whilst one can also work with an X-ray tube having a smaller focus and thereby reduce the geometric blurring of the picture.

In this article a description of the new mirror camera will be given, preceded by some remarks about mirror systems in general.

#### Historical commentary on mirror systems

The use of optical systems with mirrors is by no means new, these having been applied for centuries for astronomical purposes. Mirror systems, at least when they do not also contain refracting surfaces, are free of chromatic aberrations. There are, however, two objections, the first lying in the fact that in order to gather the reflected light, either in an ocular or on a photographic film or plate, it is necessary to place in the path of the rays a constructional element which intercepts part of the light falling on the mirror. The second objection, of a technological nature, was the difficulty to make surfaces of high reflectivity the reflective power of which does not deteriorate after prolonged use.

For astronomers the first objection mentioned is of no great consequence because for their purposes a very small field of vision suffices (less than 1 to 2 degrees) and so only a small part of the incident light need be intercepted. For other purposes,

however, as in normal photography, the field of vision required is many times greater, so that very much more light is lost. Taken together with the other objection mentioned, this was the reason why in the last century only lens systems were employed for camera optics. In fact, for a given permissible magnitude of the aberrations, no greater light-gathering power could be obtained with the mirrors than with lenses owing to the loss of light just referred to: the mirrors were not free of image errors such as spherical aberration and field curvature, and on the other hand one has learned to reduce the chromatic aberration of the lenses by using a combination of different kinds of glass.

There are two factors which in the last decade have greatly improved the chances for mirror objectives for non-astronomical purposes. The technique of producing reflectors by evaporating an aluminium coat on glass has been so far advanced that practically no reduction of reflectivity need be feared, and, secondly, a simple method has been found for almost entirely eliminating spherical aberration, the most important image error of a mirror. This latter method, discovered and worked out for astronomical application by B. Schmidt<sup>3)</sup>, is based upon the use of a correction plate of a certain profile placed in the centre of curvature of a concave spherical mirror. Thanks to this improvement it became possible to design a mirror system with a greater light-gathering power than is obtainable with a lens system, even when the field of vision is large.

The much more favourable situation thereby created for mirror optics was realized by various designers<sup>4)</sup> and led to a number of practical applications of mirror systems outside the domain of astronomy. One of these, for projection television receivers, was described in this journal some years ago<sup>5)</sup>, and in connection therewith also the fundamentals of the Schmidt optical system and the construction of the aforementioned correction plate were dealt with<sup>6) 7)</sup>. There is, therefore, no need for

<sup>3)</sup> B. Schmidt, Ein lichtstarkes, komafreies Spiegelsystem, Mitt. Hamburger Sternwarte Bergedorf 7, 15-17, 1932

<sup>4)</sup> See, e.g.:  
D. D. Maksutov, New catadioptric meniscus systems, J. Opt. Soc. Amer. 34, 270, 1944.  
A. Bouwers, Achievements in optics, Elsevier Publ. Co., Amsterdam 1946

H. Rinia and P. M. van Alphen, A new method of producing aspherical optical surfaces, Proc. Kon. Ned. Ak. Wet., Amsterdam 49, 146-149, 1946.

<sup>5)</sup> P. M. van Alphen and H. Rinia, Projection television receiver, Philips Techn. Rev. 10, 69-78, 1948.

<sup>6)</sup> W. de Groot, Optical aberrations in lens and mirror systems, Philips Techn. Rev. 9, 301-308, 1947.

<sup>7)</sup> H. Rinia and P. M. van Alphen, The manufacture of correction plates for Schmidt optical systems, Philips Techn. Rev. 9, 349-356, 1947.



us to enlarge upon this here, the more so since the mirror optical system of our X-ray camera is substantially identical with that of the television receiver described. It should be pointed out that it has been no mere accident that mirror optics has found such a ready application for these purposes, more so than for normal photography. With mirror systems much more than with lens systems,

serious complications, whereas in the other applications mentioned it is a fairly easy matter to make allowances for it.

### Description of the mirror camera

One of the new Philips installations for fluorography is illustrated in *fig. 1*, complete with the high-tension generator and the control desk, which

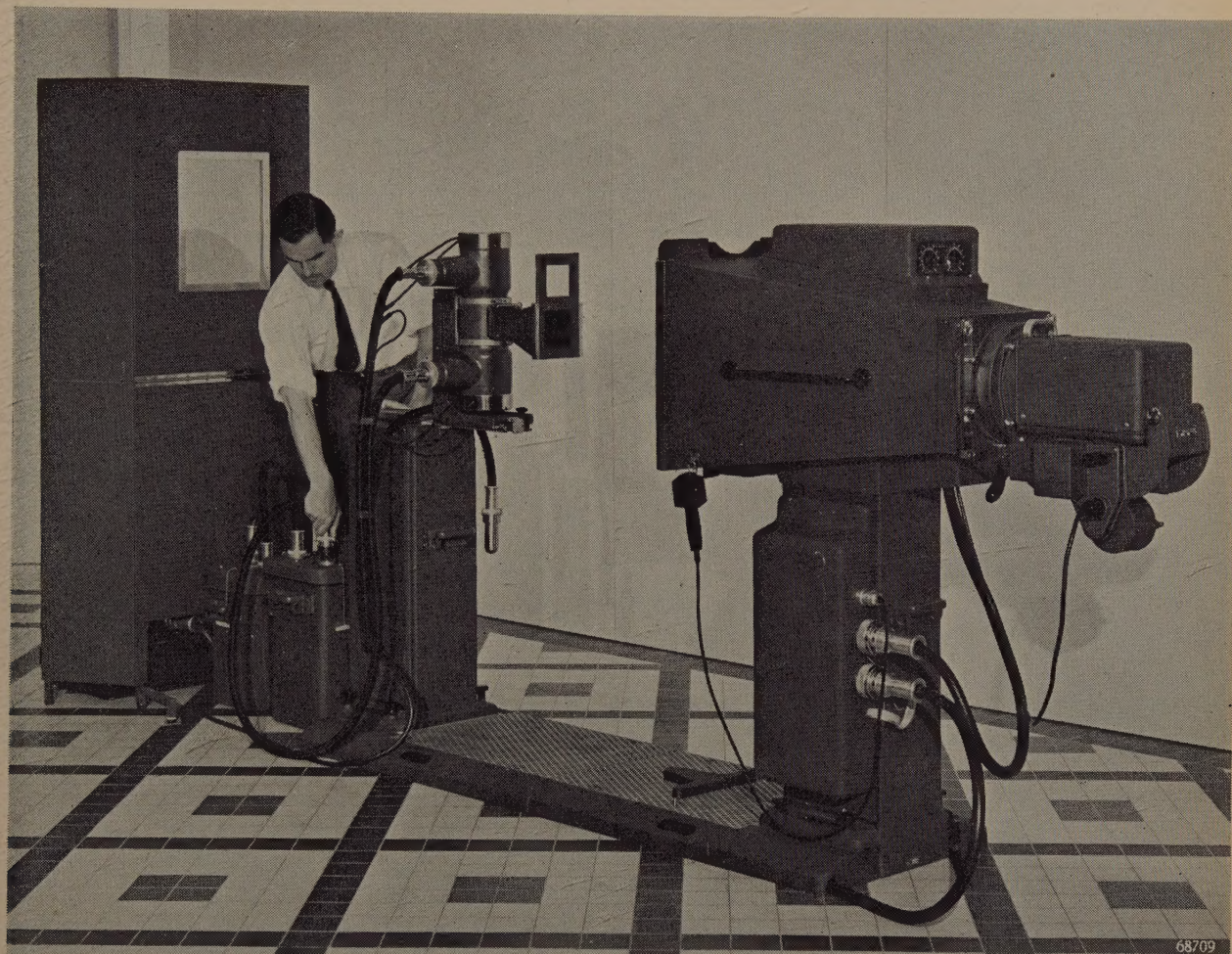


Fig. 1. Apparatus for mass chest survey by fluorography (type No. 11490). On the left the high-tension generator and control desk with metal screen for protection of the operator, in the middle the X-ray tube, on the right a light-tight hood, with fluorescent screen on the left end and the mirror camera on the right end.

the elimination of the principal aberrations can only be complete (or practically so) when the object is at a specific distance. In normal photography a certain latitude has to be allowed in this distance between the object and the camera, whereas in television projection and in X-ray fluorography, as also in astronomy, one works with a fixed object distance. Moreover, with the Schmidt optical system field curvature is not eliminated, which for normal photography would involve rather

need not be discussed here again. The patient is placed with his chest close up against the front of the "hood", at the other end of which the mirror camera is attached; *fig. 2* gives a better picture of the hood and camera.

*Fig. 3* is a diagrammatic cross section of the hood with camera. The rays of light emitted by the fluorescent screen pass through the correction plate *C*, fall on the concave spherical mirror *S* and are focused upon the sensitive surface of the film strip



$F$  in the focal plane of the optical system. The screen image of  $42\text{ cm} \times 42\text{ cm}$  is thereby minimized  $10\frac{1}{2}$  times to a size of  $40\text{ mm} \times 40\text{ mm}$ , for which a reel of non-perforated film 45 mm wide is used. The cassettes of the camera can take a reel of film of the normal length of 30 metres, on which about 600 pictures can be taken.

As already mentioned in passing, with the

of it tearing, while if it is too thin it may wrinkle. A thickness of 0.15 mm was found to be suitable.

The forward travel of the film, like all the other operating actions, is fully automatic. After the examinee has been placed in front of the camera hood and his identification card (the number on which is photographed together with the image on the fluorescent screen) inserted in a slot in the hood, all

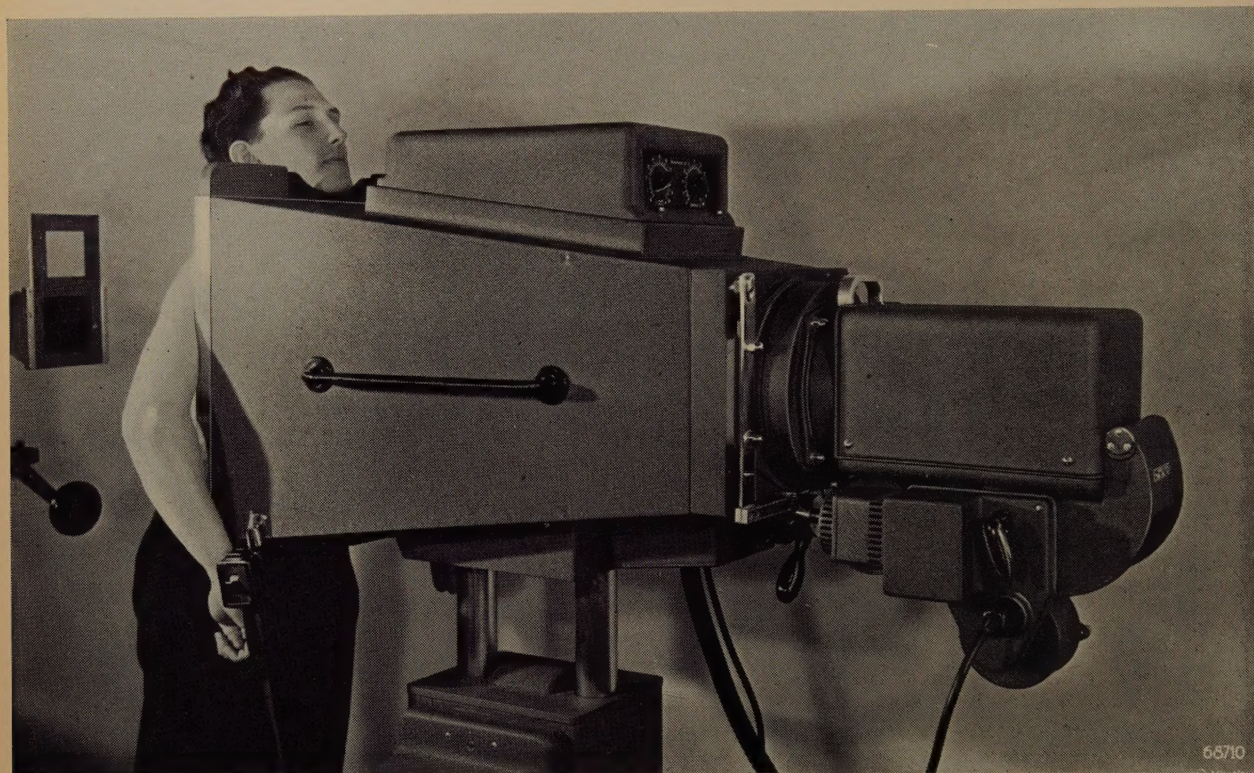


Fig. 2 The hood with mirror camera in use. When the examinee has been placed in the right position and his identification card inserted in a slot in the hood the operator has only to press a button for the photograph to be taken and everything is prepared automatically for the next one. By means of an automatic timer, seen mounted on top of the hood, the exposure is stopped as soon as a certain average density of the film is reached. The operator has only to choose one of three fixed tube voltages, according to the thickness of the examinee, and to adjust the hood and the X-ray tube to the right height.

Schmidt system field curvature is not eliminated, in contrast to what one is accustomed to with lens systems. Consequently, during the exposure, the film has to be spherically curved, concentrically with the mirror and with the convex side towards it. The film is given the required form by pressing it from behind against the square film frame with the aid of a spherically curved plate (radius of curvature 103.5 mm). At first sight it may seem surprising that this spherical deformation of the film (the material being stretched in the middle and compressed at the edges) is possible. One condition is that the thickness of the film must lie within certain limits. If it is too thick there is a risk

the operator has to do it to press in a button. The X-ray tube is thereby automatically brought into action and switched off again after the correct exposure time, the spherical "plunger" is withdrawn, the film travels one picture frame forward and is again spherically pressed out, while a locking device then comes into action preventing another photograph being taken before the identification card has been changed. This and other precautions against possible mistakes, as also the accompanying warning signals, the automatic timer (see figs 2 and 3) and other auxiliary apparatus will not be gone into here; they are described in the article quoted in footnote <sup>2</sup>),



When a new reel of film has to be put in, the entire film-travel mechanism with the film holder can be turned down. Fig. 4 shows the camera in this open position.

As to the most important property of the camera — its speed — a rough idea of this has been given above when comparing the exposure time required for lung photographs with that for the lens camera

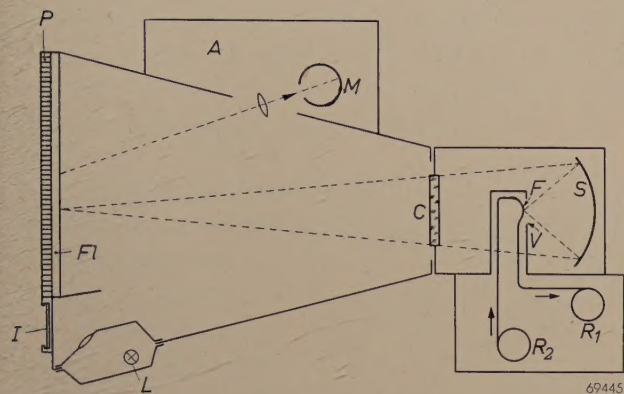


Fig. 3. Diagrammatic cross section of the hood and mirror camera. *Fl* fluorescent screen, *P* grid intercepting the scattered X-rays coming from the examinee, *S* spherical mirror, *C* correction plate, *F* film strip pressed out spherically against the film gate *V*, *R*<sub>1</sub> and *R*<sub>2</sub> rewinding and unwinding reels for 30 metres of film; *A* automatic timer with multiplier photocell *M* (this measures the luminance of a certain part of the fluorescing screen and regulates accordingly the time during which the current for the X-ray tube is kept switched on); *I* identification card, *L* lamp for illuminating this card.

formerly used. It may, however, be desired to express this in terms allowing of a direct comparison with any other cameras. For conventional photographic cameras of normal speed it is customary to quote the relative aperture  $D/f$ ;  $D$  is the diameter of the diaphragm limiting the effective beam of light,  $f$  is the focal length. We could, of course, quote this quotient also for mirror cameras, but it is to be noted that here the relative aperture is not a proper measure for their light-gathering power. Since this is a question that has already given rise to many misapprehensions, it is deemed to be of sufficient importance to go into it more closely.

#### The figure of merit of optical systems in general

The point at issue is the illumination of the focal plane and how this is correlated with the "relative aperture".

Let us suppose that the object is a luminous plane with a luminance  $B$ , placed perpendicular to the axis of the optical system, and that the object is a Lambert radiator. The rays which come from a surface element  $\Delta S$  of the object lying on the axis and which enter the optical system fill a cone the half angle of which is denoted by  $a$  (fig. 5). The luminous flux gathered by the optical system from the element  $\Delta S$  is then  $\Delta S \cdot \pi B \sin^2 a$ . This luminous

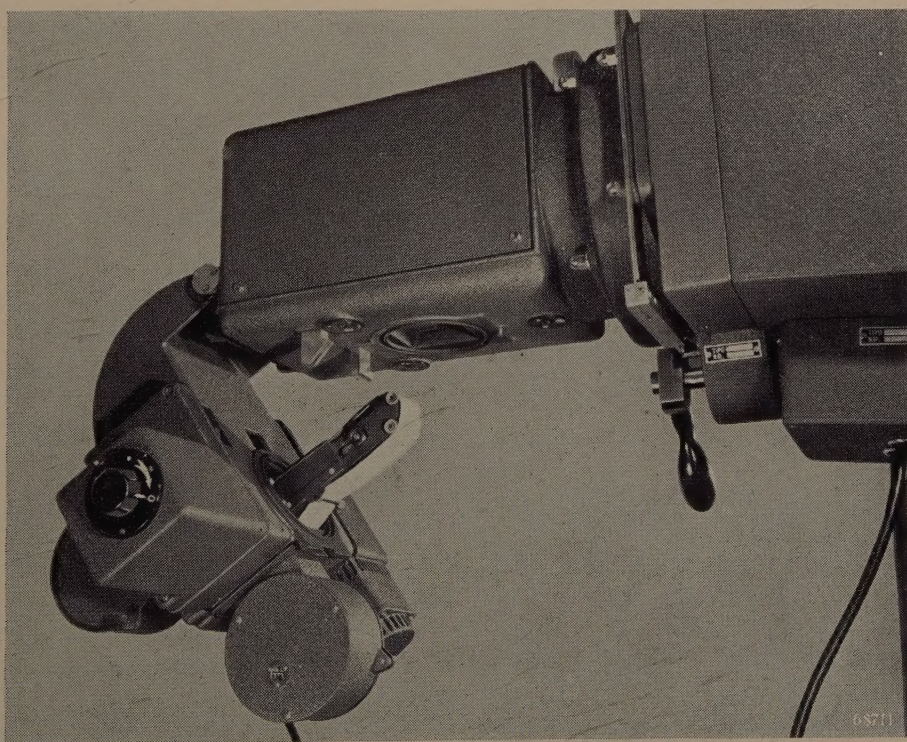


Fig. 4. The mirror camera with the film holder turned down.



flux falls in the image on an area  $\Delta S'$ , the illumination of which is thus

$$\frac{\Delta S}{\Delta S'} \pi B \sin^2 \alpha \dots \dots \dots (1)$$

Denoting the linear reduction of the projected image — the “reduction factor” — by  $r$ , then  $\Delta S/\Delta S' = r^2$ .

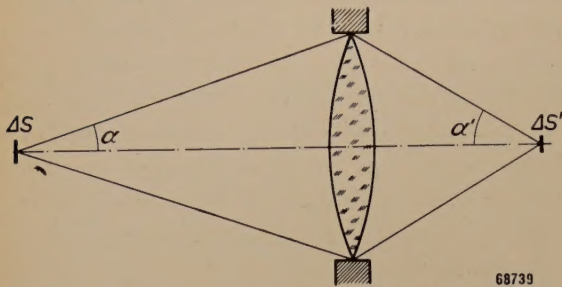


Fig. 5. The limiting diaphragm (entrance pupil) of an optical system (with lenses or mirrors) receives from a surface element  $\Delta S$  of the object a cone of light with half angle  $\alpha$ .

To conform with existing definitions we formulate the illumination on the image plane as

$$\frac{1}{4} \pi B \cdot \frac{1}{N^2}, \dots \dots \dots (1a)$$

the quantity  $1:N$ , according to the foregoing, being given by

$$\frac{1}{N} = 2r \sin \alpha \dots \dots \dots (2)$$

This quantity was called the “aperture ratio” of the optical system for the given reduction factor and was adopted in 1950 by the British Standards Institution as a figure of merit of photographic objectives. As shown by the deduction, it indicates directly the “light gathering” power of the optical system determined by the geometrical arrangement.

Often, for example in the formula given by the British Standards Institution, use is made of the half angle  $\alpha'$  of the cone of light on the image side falling upon the image plane when the optical system is focused for the reduction factor  $r$  (see fig. 5). For a coma-free optical system the “sine law”

$$\frac{\sin \alpha'}{\sin \alpha} = r$$

applies. The value  $\sin \alpha' = r \sin \alpha$  is the “numerical aperture” introduced by Von Abbe for microscope objectives (thus applying, just like the aperture ratio, only for a certain reduction factor, in this case the enlargement corresponding to the tube length and indicated on the microscope objective).

The aperture ratio  $1:N$  can be related to the relative aperture  $D/f$  in the following way. Let us first imagine the simple case of a thin, single lens with the diaphragm lying in the plane of the lens (fig. 6). Here the lens formulae apply as

known from elementary text books. For the object distance  $v$ , measured from the object to the diaphragm, thus in this case to the lens itself, we have  $v = f(r + 1)$ , and from fig. 6 it follows that

$$\tan \alpha = \frac{D}{2v} = \frac{D}{2f(r + 1)} \dots \dots \dots (3)$$

Now in all the cases that can be considered here the half angle  $\alpha$  of the light cone is so small that the tangent can be put equal to the sine. Consequently the formula for  $1:N$  can be developed into<sup>8)</sup>:

$$\frac{1}{N} \approx 2r \tan \alpha = \frac{D}{f} \frac{r}{r + 1} \dots \dots \dots (4)$$

This formula (4), derived for a thin, single lens, may likewise be applied for the composite photographic lenses. It is true that we must then take as the object distance the distance from the object to the first principal plane of the lens, but with these lenses the entrance pupil, i.e. the diaphragm, may be assumed to lie approximately in that plane, so that the formula still holds.

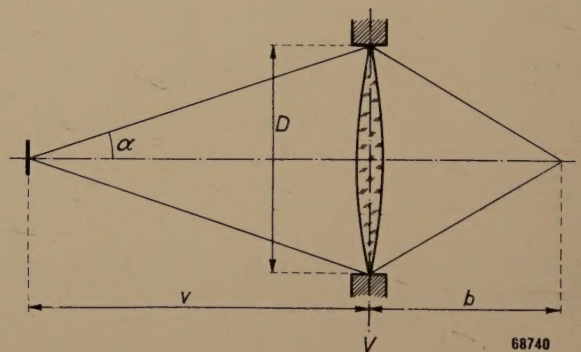


Fig. 6. Path of the rays through a thin lens.  $V$  is the first principal plane (which for a thin lens coincides with the second principal plane),  $v$  the object distance,  $b$  the image distance.

In the case of mirror systems, however, the situation is different. Here the function of the diaphragm is performed by the correction-plate holder placed in the centre of curvature of the mirror and thus

<sup>8)</sup> Without the simplification mentioned, with the aid of the known relation between sine and tangent.

$$\sin^2 \alpha = \frac{\tan^2 \alpha}{1 + \tan^2 \alpha}, \dots \dots \dots (5)$$

we find the more general equation

$$\frac{1}{N} = \frac{D}{f} \frac{r}{\sqrt{(r+1)^2 + \left(\frac{D}{4f}\right)^2}} \dots \dots \dots (6)$$

The simplification is permissible because in all systems to be considered  $D/f$  is not greater than 1.5 (the “ $f$ -number” not smaller than  $1/1.5 = 0.67$ ) and the reduction  $r$  is at least 5. Then, according to eqs (3) and (4),  $(D/4f)^2 \ll (r + 1)^2$ , which amounts to the same as  $\tan \alpha \approx \sin \alpha$  ( $\alpha < 7^\circ$ ).



lying at a distance  $2f$  in front of the mirror (which is approximately the position of the first principal plane); see *fig. 7*. In this case the distance from the object to the diaphragm is :

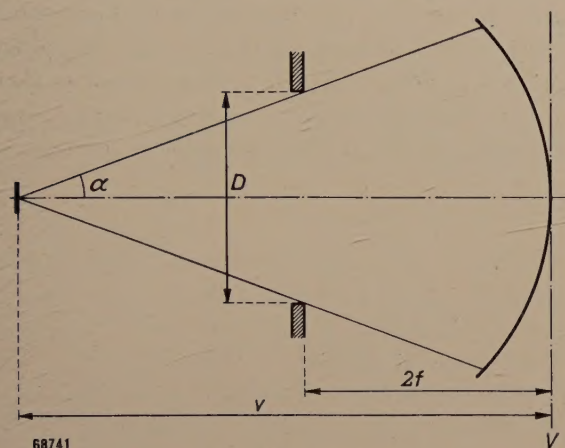
$$v - 2f = f(r+1) - 2f = f(r-1).$$

Formula (3) for the apex angle of the light cone gathered has therefore to be replaced by:

$$\tan \alpha = \frac{D}{2f(r-1)} \quad \dots \quad (3a)$$

and formula (4) — for the same simplifying supposition that  $\alpha$  is not too large — by:

$$\frac{1}{N} = \frac{D}{f} \frac{r}{r-1} \quad \dots \quad (4a)$$



*Fig. 7.* In a mirror system the limiting diaphragm is a distance  $2f$  in front of the first principal plane  $V$ . Given the same object distance  $v$  and diaphragm diameter  $D$  the angle  $2\alpha$  of the cone of light received is therefore greater than that in a lens system.

Now we are in a position to draw the conclusions for the point at issue in this chapter. It is seen that for very large object distances, i.e. very great reductions (where  $r + 1 \approx r \approx r - 1$ ), the formulae (4) and (4a) are both simplified to  $1:N = D/f$ , in other words we find both for lens and for mirror systems the well-known rule that the illumination in the image is proportional to the square of the relative aperture. In the case of relatively small reductions, as applied in X-ray fluorography,  $D/f$  alone is not, however, sufficient to indicate the light-gathering power, and especially not when comparing a mirror system with a lens system. Then the reduction factor must certainly be taken into account, and this is best done by quoting the "aperture ratio"  $1:N$ , together with the reduction factor.

Since the equation  $1:N = 2r \sin \alpha$  gives directly the light-gathering power of the optical system, it is only logical to allow for the obstruction of the film holder by including the "shadow factor"

which must always be taken into account with mirror systems and is likewise of a geometrical nature. (The importance of this shadow factor has already been pointed out in our historical commentary). As far as the illumination of the focal plane is concerned the useful cone of the entering light having the apex angle  $2\alpha$ , but being partly intercepted by the blacked-out centre of the correction plate concealing the film holder, is equivalent to a cone of light having a smaller apex angle  $2\alpha_{\text{eff}}$  and not intercepted at all. The quantity  $2r \sin \alpha_{\text{eff}}$ , again written as a fraction with 1 as numerator, will be called the "effective aperture ratio". With this number as basis it is possible to make a true comparison of the light-gathering power of lens systems and of mirror systems.

### The speed of the Philips mirror camera

Our X-ray mirror camera has a focal length of 100 mm and a diaphragm diameter (diameter of the correction plate) of 115 mm. For a reduction factor  $r = 10.5$  the aperture ratio according to formula (4a) works out to  $1:N = 1:0.79$ . The shadow factor amounts to about 0.45, which means that 55% of the light is intercepted by the film holder. Therefore the effective aperture ratio is  $1:1.17$ . This is to be compared to the aperture ratio of  $1:1.9$  for the lens system formerly used, where the reduction factor was 6 (film width 70 mm). The light-gathering power of the mirror camera is therefore  $1.9^2/1.17^2 = 2.6$  times that of the lens camera.

Apart from its geometrical light-gathering power also the losses through reflection or absorption in the parts of the optical system have to be considered. In the case of the lens system in question the lens surfaces are coated, so that the losses of light in that objective, including absorptions, are reduced to about 30%. In the mirror camera the losses in the optical system are higher, 20% of the light being lost through reflection from the surfaces of the correction plate and another 20% through absorption in the surface of the mirror. The difference, however, is almost outbalanced by the fact that when using a lens camera 20% of the light is lost through absorption in a plate of lead glass that has to be placed between the fluorescent screen and the camera in order to protect the film against the X-rays penetrating through the screen. With a mirror camera there is no need for such a plate because the X-rays are sufficiently absorbed in the metallic parts of the film holder. (X-rays are now prevented from passing through the hood walls by lining it with a thin layer of lead.)



According to the deduction given,  $(1/N)^2$  multiplied by  $\frac{1}{4}\pi B$  and by a transmission factor allowing for the losses of light just mentioned gives at once the illumination on the film. This, however, only holds for the centre of the field of vision. Towards the edges of the image the illumination diminishes through various causes, such as owing to the fact

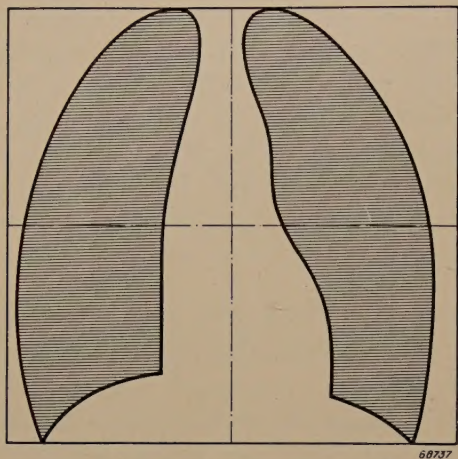


Fig. 8. Position of the lungs in a chest photograph.

that light beams striking the objective at an angle are limited not only by the diaphragm but also by the holders of the lenses or the mirror. This effect, which is known under the name of vignetting, is of less consequence in the mirror system than in lens systems. This is particularly of importance when taking photographs of the lungs, because the physician is less interested in the middle portion of the picture on account of the fact that most affections of the lungs occur in the outer parts. Taking, by way of example, as the representative part a zone at about  $\frac{1}{4}$  of the edge of the field of vision (fig. 8), with the lens system the illumination

is reduced to 45%, whereas in our mirror system it is reduced to 70% of that in the centre.

The luminance  $B$  of the fluorescing screen, which together with the light-gathering power of the optical system determines the illumination on the film and thus the exposure time required, depends upon the hardness and intensity of the X-rays and upon the thickness (absorption) of the examinee. For practical purposes it is desired to express the necessary exposure time directly as a function of these two variables. This has been done in the graph of fig. 9, plotted from data collected in the periodical chest survey of Philips' personnel at Eindhoven<sup>9)</sup>. It applies for a suitably chosen combination of film, fluorescent screen and scattered-ray grid: the same power was fed to the X-ray tube at all voltage steps. It is seen that with the examinees divided into three thickness groups, for which tube voltages of respectively 70, 85 and 100 kV are chosen, all photographs can be taken with exposures lying between 0.04 and 0.20 sec.

### The size of the photographs

It has been seen that the mirror camera is constructed for 45 mm film, whereas for the lens camera described earlier a 70 mm film was used. The reasons for this change of film size are as follows.

To judge the relative merits of the two sizes there are three main aspects to be considered:

- 1) Considering that the basic idea of fluorography is to save material and other expenses, it is only logical to choose the smallest size of picture. This, however, is not the deciding factor when a comparison is made with full-size radiography, because with the 70 mm film the cost of the photographs is already so far reduced that the size no longer plays an important part anyhow. However, in the case of mass chest survey, where full-size pictures are prohibitive, the 45 mm film size offers an appreciable saving in film cost (about 50%) compared with the 70 mm size.
- 2) In favour of the larger size it might be mentioned that the pictures could then, if necessary, be examined with the naked eye. But for a critical examination both the 70 mm and the 45 mm pictures have to be magnified either with a magnifying glass or with a projector.
- 3) Finally there is the important point of the quality of the picture. If the picture is excessively small the (relative) definition is affected by the granulation of the film, and that is why we no longer use the 35 mm film which was at first em-

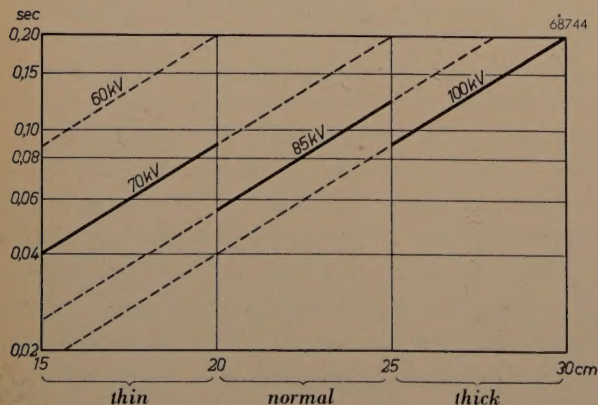


Fig. 9. Exposure times for chest photographs taken with the 45 mm mirror camera, as a function of the thickness of the examinee, for three tube voltages. The power applied to the tube is in all cases 14 kW; the distance from the X-ray focus to the fluorescent screen is 90 cm; fluorescent screen Levy West 48, film Gevaert Scopix G.

<sup>9)</sup> G. C. E. Burger, not published.



ployed for fluorography and which gave pictures no more than 24 or 30 mm wide. With the size of 45 mm now chosen there is no trouble from granulation provided one of the very fine-grained makes of film is used which are now available on the market. It is true that for a still larger size of picture and

also necessary to work with a larger focal length, as is to be understood when considering the size of the field of vision, which is roughly given by the quotient of the image diagonal and the focal length, and with our 45 mm camera amounts to about  $25^\circ$ . The field of vision is limited by the occurrence of

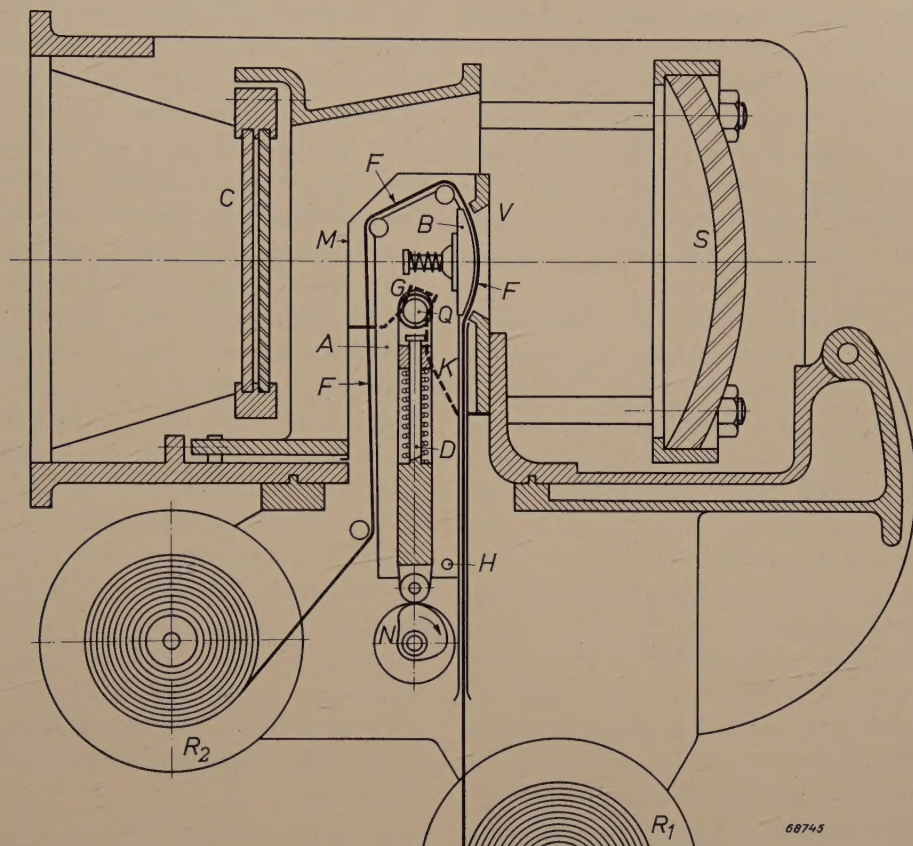


Fig. 10. Longitudinal cross section of the mirror camera. The drawing is still greatly simplified; in particular, all details of the automatic film travel and the locking and signalling devices coupled therewith are omitted. In addition to the parts already discussed, such as the mirror *S* and the correction plate *C* — which are shown here in their right proportions and distances — the drawing shows some details of the film holder and the device for spherically pressing out the film. *V* fixed film gate, onto which is fixed a cap *K* with oblique slot *G*; *A* arm, rotating about a spindle *H*, carrying the rollers guiding the film *F* and to which is attached, behind the path of the film, the spherical pressure plate *B* with ball joint. By the action of a cam disc *N* and rod *D*, via a spring, the roller *Q* is forced upward; as it moves upward this roller slides in the oblique slot *G*, thereby displacing the entire arm *A* towards the film gate and pressing the film, via the spherical pressure plate, against this gate with a force of 16 kg, so that the film assumes a spherical shape in the opening. Except for the film gate *V* the arm *A* with the film is sealed off light-tight by a metal housing *M*.

the same sharpness of definition a coarser-grained film could be used, thereby taking advantage of the higher sensitivity of a coarse-grained emulsion and thus allowing a shorter exposure time, but this type of film is not normally available.

It is technically quite possible to construct a mirror camera for larger size pictures<sup>10)</sup>. Then it is

aberrations of a higher order when the angle is larger. Taking the same permissible field of vision, a 70 mm camera would require a focal length roughly  $70/45 \approx 1.5$  times that required for the 45 mm one. And since the correction plate and the mirror would then have to be given a correspondingly larger diameter in order to get the same relative aperture  $D/f$ , this would inevitably lead to a much larger and heavier, and thus more expensive, construction than that of the 45 mm size.

It is an open question whether the medical world will consider the somewhat easier examination of

<sup>10)</sup> A mirror camera for 70 mm film was built some years ago in Denmark; see Amer. J. Röntg. Rad. Therapy **59**, 416-419, 1948. A more recent construction of a 70 mm camera is that of A. Bouwers (Fortschr. a. d. Geb. Röntgenstr. **74**, 578, 1951, No. 5).



70 mm pictures of sufficient importance to justify the much greater expense (and less easy transportation!) of a 70 mm camera for mass chest survey.

### Construction of the camera

Fig. 10 is a simplified cross-sectional drawing giving an idea of the mechanical construction of the mirror camera described here. It has already been said that we shall not deal here with the provisions made for the forward travel of the film, etc., which do not differ essentially from those found in the lens camera. We shall discuss only some constructional problems inherent in the designing of the mirror camera.

The position of the film with respect to the mirror is highly critical, a displacement of 0.02 mm in the axial direction already being sufficient to cause a perceptible reduction in the definition of the picture. This is related to the very large aperture ratio of the camera (very large angle under which the rays merge upon a focal point). A very robust construction and most precise finishing of the mechanical parts bearing the film and the mirror proved to be not sufficient to guarantee the proper distance: it was found necessary also to eliminate the effect of thermal expansion of those parts. To this end use was made of metals having different expansion coefficients, a measure such as is taken, for instance, in the construction of time-pieces to ensure that the length of the pendulum remains constant. The camera housing, in which the correction plate with a holding ring is mounted and to which the film holder is hinged (at the other end) — see fig. 10 and also fig. 4 —, has been made of an alluminium alloy; the spherical mirror is attached to the sup-

porting flange of the correction plate with four steel rods and has no other further supports (see fig. 11).

An axial displacement of 0.02 mm of the film corresponds to a displacement of  $r^2 \times 0.02 \approx 2$  mm of the fluorescent screen. The distance from the mirror system to the screen is therefore much less critical and there is no need of any special measures for compensating the thermal expansion of the hood keeping the camera at the correct distance from the screen (fig. 3). To give the latter distance the right value, taking into account the small differences occurring between various specimens of the camera in respect to the position of the film holder, the length of each camera is matched to the fixed length of the hood with the aid of spacing rings. This is done on a sort of optical bench, whereby the path of the rays is reversed to that in actual use: a film strip with a test pattern is put into position and strongly illuminated, the optical system projecting a  $10\frac{1}{2}$  times enlarged picture of that pattern onto a screen, the position of which is adjusted until the picture is properly focused. From the final position of the screen it can then be calculated how many spacing rings are required for a given length of hood. At the same time if there are any aberrations in the projected picture the mirror system can be adjusted, for which purpose the holder of the correction plate is fitted with a number of set screws.

It is to be noted that either a blue or a green fluorescing screen can be used at the same distance from the camera. This is not possible with a lens camera because, as already stated, when a lens camera is used a lead glass plate has to be placed between the screen and the camera, and owing to the difference in the index of refraction for the two colours there is then a difference in the optical distance.

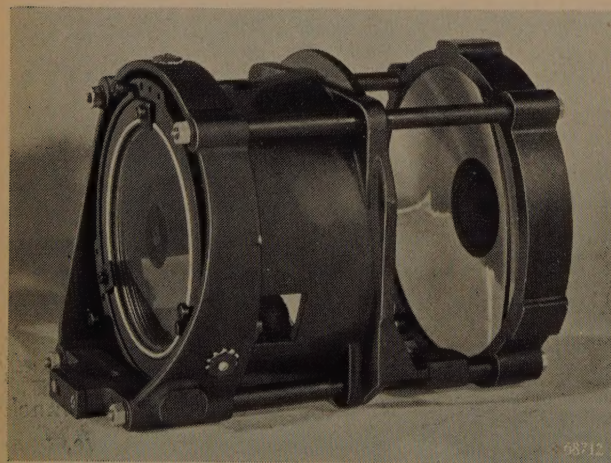


Fig. 11. The spherical mirror (on the right) is attached to the flange carrying the correction plate (on the left) with four steel rods.

A detail of mechanical interest in the mirror camera is the device for the spherical deformation of the film. The construction of this device and that for the forward travel of the film, which have to be kept as small as possible to limit the shadow factor, is shown in fig. 10. The film holder is in the form of a pivoted arm carrying the convex pressure plate (B) and the rollers for guiding the film. The arm is turned away from or towards the fixed film frame by the action of a roller sliding in an oblique slot. This to and fro movement of the roller, which thus releases the film to be carried forward and then presses it out again, is brought about via a cam disc by the small motor which also drives the wheels for the forward travel and the rewinding reel.



Non-perforated film is used in order to make use of its full width as far as possible, but this has the drawback that the possibility of it slipping during transportation is not precluded. Therefore, in order to avoid two pictures overlapping entirely or partly, a safety device is provided which momentarily closes a contact as soon as the film has been carried 50 mm forward. The next picture cannot be taken until this has been done. Should the contact not have been closed at the end of the forward travel then the relay switching on the X-ray tube is blocked and a warning signal is given by a lamp. The forward travel mechanism can then be brought into action again by pressing a button.

After 30 pictures have been taken the apparatus punches a mark in the edge of the film, so that certain parts of the reel of film can easily be identified in the dark room and, if desired, developed separately.

Results

As explained in the foregoing, the new feature about the Schmidt mirror systems lies in the fact that the aberrations of a spherical mirror can be almost entirely eliminated within a relatively large field of vision. Therefore when judging the performance of a mirror camera it is necessary not only to know the light-gathering power of the system (see above) but also to ascertain in how far the picture

is indeed free of aberrations right up to the edges. For this purpose, with each specimen of the mirror camera a series of photographs are taken of a test plate put in the position of the fluorescent screen and containing a large number of identical test pictures spaced over the entire area (see *fig. 12*). Each test picture consists of six groups of lines with respectively 6, 12, 18, 24, 30 and 36 lines per cm (*fig. 13*). With the aid of a magnifying glass

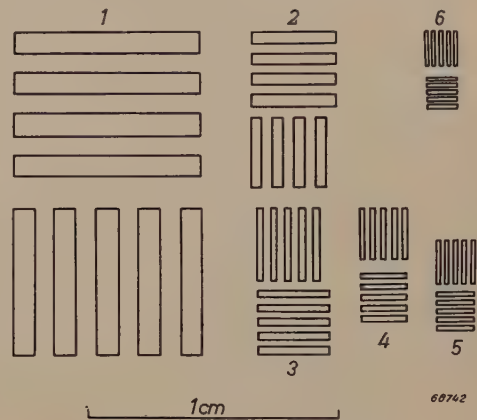


Fig. 13. Each test picture has six groups of lines, some vertical and some horizontal, with densities of respectively 6, 12, 18, 24, 30 and 36 lines per cm.

the photograph is examined, for each of the test pictures, to see which group of lines is just “resolved”, the results then being recorded on an inspection form. Should the results obtained make it necessary, the camera can then be readjusted. The results of such a test, which may be taken as being representative for the 45 mm mirror camera, are shown in *fig. 14a*. *Fig. 14b* shows the results for a representative specimen of the lens camera obtained in the same way. It is seen that in the centre of the field both cameras completely resolve all groups of lines but that towards the edges the resolving power of the mirror camera is on the whole better. Whereas, with lens cameras, in the parts of the picture which are most important from the medical point of view the resolution is limited by the inaccuracy of the lens optics, with the mirror camera the screen is the limiting factor. The mirror camera is, moreover, practically free of astigmatism, which is rather marked in the case of the lens camera.

From the photograph of the test plate reproduced in *fig. 12* it is seen that after the spherically pressed-out film has returned to its plane the picture shows practically no barrel distortion.

Every camera leaving the works is accompanied by a photograph of the test plate made with that camera on the kind of film customarily used for

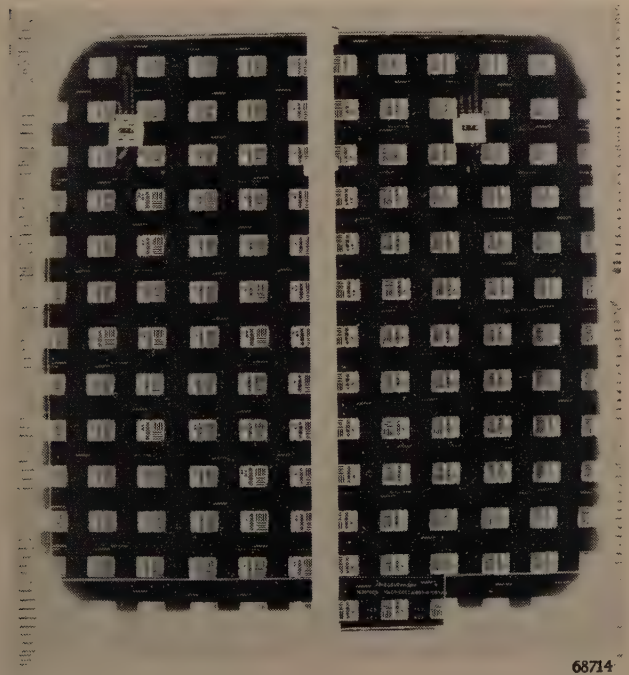


Fig. 12. Test plate with which the resolving power of each camera is tested. It has a large number of test pictures, produced photographically, each containing six groups of lines of different fineness; see *fig. 13*.







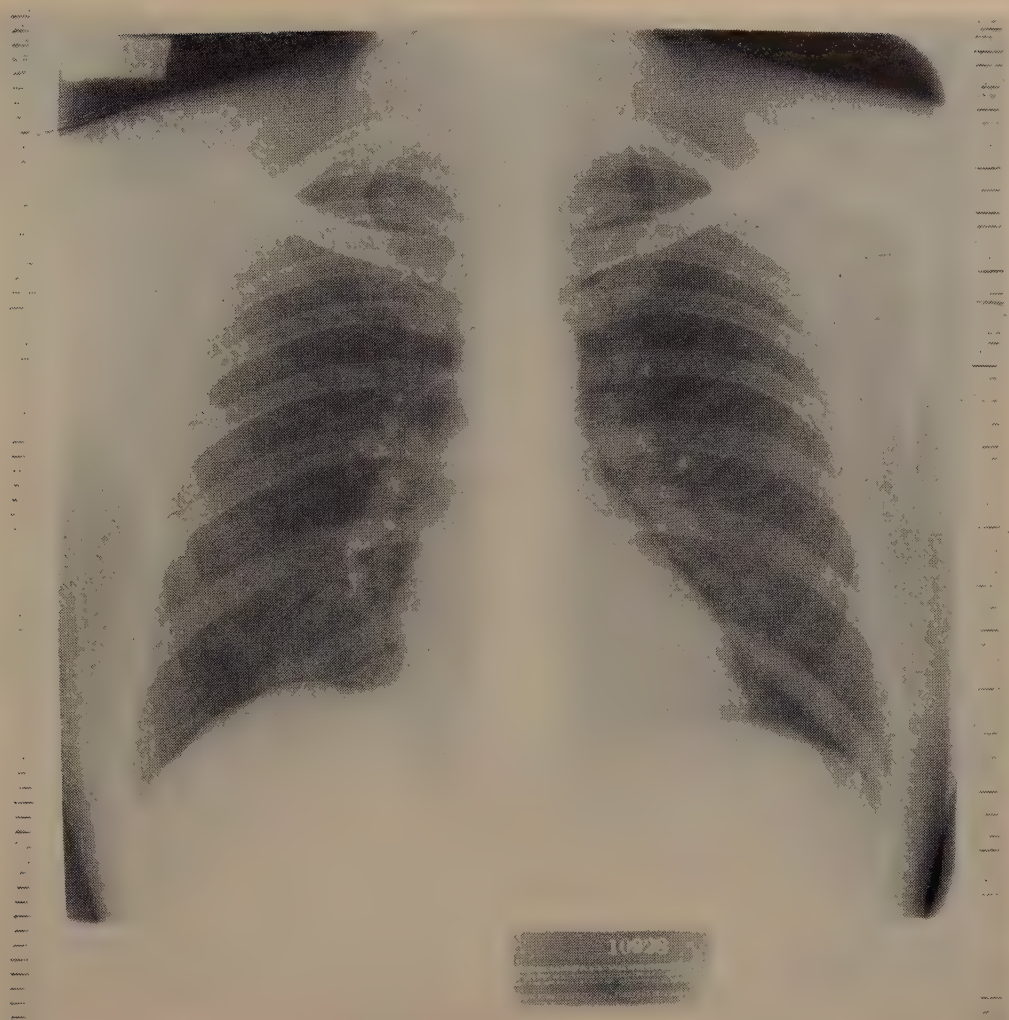


Fig. 15. Reproduction of a lung fluorogram made with the 45 mm mirror camera on Gevaert Scopic G film and then enlarged 3 times. (The reproduction of the original cannot give a quite true idea of the quality.)



## GEIGER-MÜLLER COUNTERS

by N. WARMOLTZ.

537.542:539.16.08:621.387.424

*The time when Geiger-Müller counters were used only in laboratories is now past. At the present day this instrument is being employed not only for measuring radioactivity in nuclear-physical research and in the production of nuclear energy but also as an indicator to give warning of danger from radioactivity, for example in civil and military defence. Furthermore, it forms an indispensable part of the equipment of prospectors for radioactive ores. The fact that it has become possible to make with such a sensitive instrument a measuring apparatus sufficiently robust and small for many of these purposes is due in part to the discovery of the influence that certain admixtures in the quenching gas, such as the halogens, have upon the properties of a radiation counter tube.*

### History of the radiation counter tube

The indication of individual elementary particles, atomic nuclei and radiation quanta by means of the discharge phenomena they can bring about in an electronic discharge tube — in principle consisting of a vessel filled with gas and containing two cold electrodes — dates back to 1908, when Rutherford and Geiger succeeded in counting alpha particles with such a device. The type of counter tube used by those investigators has since then been greatly improved upon, as a deeper insight was obtained into processes taking place inside the tube. In this article the historical development of the counter tube will be reviewed and some new counters produced by Philips as a result of that development will be discussed.

The first counter tube made by the investigators mentioned closely resembled in outward appearance the form of the tubes used today. It was a cylindrical tube with two coaxial electrodes of circular cross section (*fig. 1*), the outer one serving as cathode and the inner one, in the form of a thin wire, as anode. The inter-electrode potential was about 1300 V, and the tube was filled with carbon dioxide or air under a pressure of a few cm Hg. The following is the mode of operation of their counter.

The alpha particles to be counted are admitted into the tube through a very thin mica window or through a cock with a large bore connected to a partially evacuated space in which the specimen of the radioactive substance is placed. As an alpha particle enters the tube it collides with and ionises a number of gas molecules. Under the influence of the electric field the electrons thereby released migrate towards the anode wire and mainly in its vicinity form a number of ions and electrons. All the charged particles thus created are attracted by the field towards the electrodes and produce a pulse

across a load resistor; Rutherford and Geiger employed an electrometer for registering this pulse. The next alpha particle entering the tube produces another pulse, and thus the particles can be counted by counting these pulses.

No self-sustained discharge existed in the tube, the number of ions formed by the alpha particle entering the tube being simply multiplied by a certain factor.

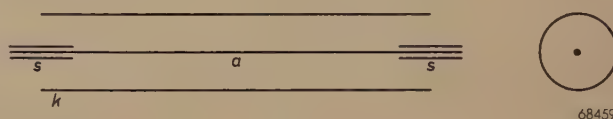


Fig. 1. Representation of a Geiger-Müller counter tube: *a* anode wire, *k* cathode cylinder, *s* screening caps for the ends.

The strength of the pulse depends, i.e., upon the position and the angle of incidence of the alpha particle in the tube, these factors influencing the paths described by the particles. To reduce this dependency Geiger and Rutherford changed the shape of the counter tube, making it spherical instead of cylindrical; a small ball acting as anode was placed in the centre of a semi-spherical cathode. The gas filling was helium under a pressure of about  $\frac{1}{3}$  atm. and with this gas under such a relatively high pressure it was possible to obtain the desired multiplication of ions at relatively low potentials.

With this apparatus and the electrometers that were available at that time only alpha particles could be counted, the ionisation caused by beta and gamma rays being insufficient in spite of the multiplying action of the gas. In 1913, therefore, Geiger proceeded to raise the pressure of the gas and applied higher voltages via a large resistor in the supply circuit for the tube. In addition, a higher field strength was obtained inside the tube



by giving the electrodes a suitable shape; the cathode was given the form of a sharp point facing a flat plate acting as anode. The gas filling was air under atmospheric pressure; the voltage was 1000 to 1800 volts. As a result of all these changes the initially formed ions and electrons were multiplied to such an extent as to give rise to a self-sustained gas discharge, but (as was essential for the purpose) this discharge possessed the property of quickly quenching itself, so that another pulse could be registered before the next particle entered the tube.

With such a counter also beta and gamma rays could be detected, but it was not possible to distinguish one kind of particle from another because the height of the pulse across the load resistor was determined only by the properties of the self-sustained discharge and not by the nature of the ionising particle. This tube was practically free from directional effects.

The pointed cathode was difficult to make in a reproducible manner and was therefore subsequently replaced by a very small sphere. The anode retained its shape of a flat plate. Still later, Geiger and Müller reverted (in 1928) to the cylindrical arrangement, with air filling (5 cm pressure), and applied voltages which were higher than the starting voltage of a self-sustained discharge. The anode wire was strongly oxidized to facilitate quenching of the discharge.

Thus there arose in principle the construction of the Geiger-Müller counter as used at the present day.

In the years that followed there appeared a great variety of counter tubes, mainly distinguished one from the other by the nature of the gas filling and the processing of the electrodes. In order to judge the effect of the gas filling we have to consider the processes taking place in the gas when an ionising particle enters the tube. It was not until good use had been made of the counter tube for a number of years that a closer insight could be obtained into the nature of these processes, and even at the present day not all the problems arising have been satisfactorily solved.

### The use of a gas discharge for detecting and counting particles

Let us consider a cylindrical counter having an anode wire and filled with a gas suitable for counting. The counter is exposed to a constant and not too strong radiation. Through ionisation of the gas molecules a particle entering the counter forms a number of pairs of ions and electrons along its path. The charge formed per cm of the particle's

path under a specific pressure depends greatly upon the nature of the particle and its velocity. The total charge is determined by the length of the path in the counter, which length depends upon the dimensions of the counter and also upon the position and angle of incidence of the particle.

When a voltage  $V$  smaller than the ionisation voltage  $V_i$  of the gas is applied between anode and cathode, via a resistor, then — excepting the losses through recombination — only the ions and electrons formed by the ionisation are collected at the electrodes. Even if the voltage were raised to several times  $V_i$  very few new ions and electrons would be formed in the counter because the velocities reached by the electrons are mostly too low. The arrival of the ions and electrons on the electrodes can be observed as a pulse  $S$  across the afore-mentioned resistor with the aid of a sensitive amplifier. Given the geometry of the counter and the source of radiation, the pulse height is an indication of the nature and velocity of the particle; if its nature is known then its velocity can be determined, and vice versa.

The higher the voltage applied to the counter, the smaller are the losses through recombination, and thus the greater is the pulse  $S$ , but once the recombination has been reduced to a negligible amount, the value of  $S$  remains constant even though  $V$  is raised further. The voltage at which this takes place depends upon the shape of the tube and the gas filling.

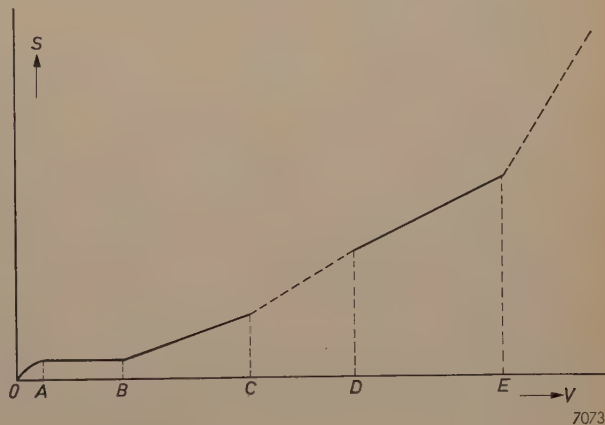


Fig. 2. Characteristic of a counter tube for constant and not too intensive radiation, showing the amplitude  $S$  of the pulses produced, as a function of the supply voltage  $V$ . In the range  $OA$ , owing to recombination, not all the ions formed by an incident particle or quantum are collected at the electrodes, whilst in the range  $AB$  such is indeed the case.  $OAB$  is said to be the range in which the tube functions as an ionisation chamber. From  $B$  to  $C$  the pulses are amplified as a result of ionisation of the gas by the electrons formed in the tube ("proportional range"). From  $C$  to  $D$  other processes begin to play a part, thereby reducing reproducibility.  $D$  corresponds to the voltage for a self-sustained discharge,  $DE$  is the Geiger-Müller range in which the discharge is quenched after a short time, while beyond  $E$  a continuous discharge occurs.



At these low voltages (some tens of volts) the counter tube is said to function as an ionisation chamber. The diagram in *fig. 2* represents the relation between the pulse height and the voltage applied to the counter tube. The part *OAB* of the curve corresponds to the range described above.

While current passes through the tube, the voltage across the tube is of course lower than the supply voltage owing to the voltage drop in the load resistor. In the case of an ionisation chamber, however, this voltage drop is negligible on account of the very small current intensity.

To give an idea of the sensitivity of a counter tube functioning as an ionisation chamber, it is to be noted that in air of 1 atmosphere pressure an alpha particle of 3.3 MeV forms about  $5 \times 10^4$  pairs of ions and electrons per cm of the path length. Assuming the length of the path traversed by the particle in the chamber to be 1 cm, this means that a charge of  $8 \times 10^{-15}$  coulomb flows to the electrodes. The peak value of the voltage across the series resistor produced by this charge can be roughly calculated by assuming that the whole of the charge is used in charging the capacitance parallel to the resistance. For a capacitance of 10 pF (the value usually given to the input capacitance of an amplifier connected to a counter tube) we then arrive at a voltage of about  $8 \times 10^{-4}$  V. For an electron (beta particle) entering the counter tube with an energy of 1 MeV the number of ion-electron pairs formed is about a factor 1000 smaller, and thus the pulse has a value of  $8 \times 10^{-7}$  V. The inevitable noise of the amplifier will amount to, say,  $10^{-5}$  V. It is obvious that an alpha particle can be detected but not a beta particle.

When the tube voltage is raised an increasing amount of excitation and secondary ionisation of the gas molecules is produced by the electrons accelerated in the field, with the result that a greater charge is accumulated at the electrodes and the pulse becomes greater. In this way it is possible to reach an amplification up to 1000 times. Then the range *BC* in *fig. 2* is reached and we have the Rutherford and Geiger counter. In this range (as also in the lower tube-voltage ranges) the pulse height is proportional to the number of ions initially formed by the particle entering the tube. Counters operating particularly in the range *BC* have therefore been given the name of proportional counters; they are distinguished from the ionisation chamber in that they have a multiplication factor largely exceeding unity. What has been mentioned in connection with the ionisation chamber about direction-dependency and the nature of the par-

ticles to be counted applies also to these proportional counters. In this range, too, the tube currents are so small that there is hardly any drop in the tube voltage when the tube is conducting.

By raising the voltage higher the range *CD* is reached. Apart from the ionisation by electrons other processes then begin to play a part, especially the release of electrons from the cathode by the positive ion bombardment and by the impact of radiation emitted by excited gas molecules as they revert to their original state. The total amplification becomes very high, but only at the cost of reproducibility, so that this range is less suitable for quantitative measurements.

When the voltage is higher than that corresponding to point *D* in *fig. 2* a self-sustained discharge takes place as soon as the incident particle causes some ionisation in the gas. The voltage corresponding to point *D* is called the starting voltage for a self-sustained discharge. The current strength of the discharge does not depend upon the number of ions initially formed, i.e. not upon the nature of the particle entering the counter, but upon the voltage applied to the tube and also the value of the load resistor, since the voltage drop across this resistor is then no longer negligible, so that it partly determines the tube voltage during the discharge.

For the following particle to be detected it is necessary that the self-sustained discharge should be quenched before that particle enters the counter. As will be shown later, with some gas fillings this quenching takes place spontaneously provided the load resistor has a certain minimum value, but with other counters quenching is brought about by lowering the tube voltage after each discharge by means of a special circuit. Hence these counters also produce pulses. These pulses are mostly of longer duration than those produced by a proportional counter; the multiplication of the initially formed charge, however, is much greater, viz. about  $10^7$  times. It is this range that is invariably used in Geiger-Müller counters<sup>1)</sup>. An electron of 1 MeV can produce pulses of 1 up to 100 V across the load resistor.

When the voltage is raised above the value corresponding to the point *E* in *fig. 2* the counter is no longer self-quenching and the self-sustained discharge is very difficult to quench even with the aid of the usual simple circuits. This range is therefore never used for counting purposes.

<sup>1)</sup> In literature, for the sake of brevity, these are often referred to as Geiger counters, but considering their historical development the name Geiger-Müller counter is to be preferred.



The following comments will be confined to the Geiger-Müller counters, the ionisation chamber and the proportional counter being left out of consideration although these are also used for many purposes.

### Properties of the Geiger-Müller counter

So far we have spoken only of the amplitude of the pulses produced by amplification of the initially formed charges. Now we shall consider to what extent the number of pulses given by the Geiger-Müller counter is a correct measure for the number of particles entering it. As will presently be seen, generally speaking not every particle entering produces a pulse; owing to various causes the efficiency of the counter is less than 100 %.

In the first place it is found that the tube voltage has little effect upon the efficiency of many Geiger-Müller counters. When plotting as a function of the tube voltage the number of counts per unit time given by a Geiger-Müller counter exposed to constant radiation, a counting characteristic as shown in *fig. 3* is obtained (for a radioactive source of moderate strength). Within the

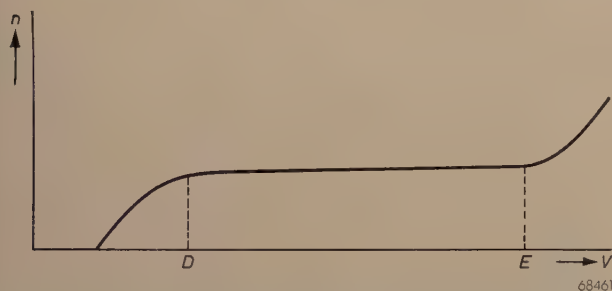


Fig. 3. Counting characteristic of a Geiger-Müller counter. Plotted along the ordinate is the number ( $n$ ) of particles counted per unit time in the case of a constant radiation, and along the abscissa the voltage  $V$  in the tube circuit. The range  $DE$  (these letters have the same meaning as in *fig. 2*) is called the plateau of the tube.

range  $DE$ , already defined above, the counting rate depends but little upon the applied voltage (often increasing slightly in a linear manner as the voltage is increased). The range  $DE$  is called the plateau of the counter tube, and for measuring purposes the supply voltage is usually chosen somewhere within this range. The slope of the plateau is expressed by the relative increase in the counting rate per 100 V increase in applied voltage. For a good counter it is customary to specify a plateau slope smaller than 10% per 100 V. The length of the plateau should be at least, say, 100 V.

In connection with these requirements it is well to take into account the manner in which the counter is to function. Let us take, for example, a counter tube having a plateau slope of 10 % per 100 V. When the tube voltage (of about 1000 V) is stabilized to within 1 volt (as is easily done) then,

with a constant radiation, the voltage variations cause a variation of no more than 0.1% in the number of pulses per unit time. This is much less than the uncertainty in the various measurements due to changes in the geometry of the set-up of counter tube and specimen, which often amounts to a few per cent even though the utmost care is taken. When stabilized voltages are employed a plateau slope greater than that mentioned above might therefore suffice, but if the voltage source is not stabilized or the counter is fed from batteries (which always show a gradual voltage variation) then of course a fairly flat plateau is desired. A small slope is also of importance for counters whose plateau becomes displaced in its entirety during their lifetime; with good counters, however, this hardly ever happens.

The small slope of the plateau of a Geiger-Müller counter is due partly to the special form and arrangement of the electrodes. With a counter tube consisting of two plane parallel plates the closer the formation of the ion pairs by the incident particle is situated to the cathode the greater is the chance of a discharge taking place, because then the distance travelled by the electrons and thus the chance of new ion pairs being formed is greater. The higher the voltage the greater is the volume within which the primary ion pair may be formed to give a certain probability of initiating the discharge. Thus, with a constant radiation, the number of particles counted increases with the voltage, and this means a considerable plateau slope. With the cylindrical arrangement of the electrodes and the gas fillings commonly used, however, the area of high field strength is concentrated about the anode wire and the electrons formed by the incident particle ionise the gas only in the vicinity of that wire. Except for the few electrons formed very close to the anode wire or those which occur at the free ends of the counter tube, all the electrons traverse the favourable area and so have the same chance of forming new ion-electron pairs and thus a discharge. Disregarding the very beginning of the plateau, this chance does not depend upon the voltage, and this means a small plateau slope. (With some gas fillings some of the electrons formed at a distance away from the anode wire are "captured"; this reduces the sensitivity of the counter, but the slope of the plateau remains small.)

The fact that, nevertheless, the plateau is not always flat is due to the following causes:

- 1) The occurrence of secondary discharges. Sometimes the discharge initiated by the incident particle leaves behind in the counting tube so many residual charges or molecules in an excited metastable state (possibly on the surfaces of the electrodes) that sooner or later there is a chance of a second discharge pulse being formed. The higher the volt-



age the greater is the chance of these secondary discharges occurring. Of course the circuit employed is also of importance in this respect.

2) End effects. The higher the voltage the larger is the area at the free ends of the tube where an electron has a certain chance of forming a discharge, as a consequence of which the "sensitive volume" and thus the number of counts is increased.

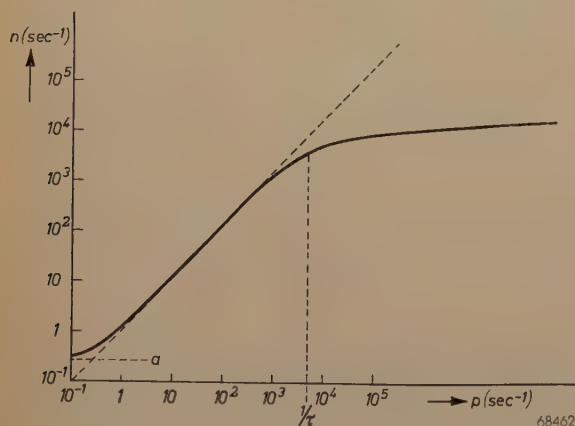
Provided the radiation is not too strong the efficiency of a Geiger-Müller counter is hardly affected by the intensity of the radiation. It is, however, strongly influenced by the nature of the particles and by the construction of the counter tube. Counters for soft radiation (beta particles with very low energy; soft X-rays) are therefore often fitted with a window having a low absorption factor (mica window) and the composition of the gas filling is so chosen that the particles or quanta have a good chance of ionising the gas molecules<sup>2</sup>). Counters for hard gamma rays, on the other hand, are preferably made with a wall of a heavy metal, for instance lead, in which the gamma quanta have the greatest probability of releasing electrons, which in turn ionise gas molecules. The efficiency of such a counter is much lower.

For very weak and very strong radiations the efficiency of Geiger-Müller counters is, however, no longer constant. This is illustrated in *fig. 4*, where the number of counts recorded per unit time has

been plotted as a function of the number of particles (e.g. electrons) entering the counter per unit time. For the sake of simplicity it is assumed that with an average intensity of radiation the efficiency is exactly 100 %, the slope of the line at that point then being 45°. With a low radiation intensity a greater number of counts are recorded than correspond to one pulse per incident particle. This is because a certain number of pulses is always recorded even though no source of radiation has been brought into the vicinity. These are referred to as "background". Obviously this background is of the greatest importance when measuring weak radiations, but still its presence does not preclude the possibility of measuring weak radiations accurately, as will be seen from the following. Let the number of counts due to the background during a certain period be  $B$  (this number can be counted) and the number of counts to be ascribed to the radiation source during the same period  $L$ . Then the total number of counts registered is  $B + L$ , from which  $L$  can be calculated. Now, owing to the statistical distribution of the instants at which the pulses are produced, in the sum  $B + L$  there is an error proportional to  $\sqrt{B + L}$ . The relative error in  $L$  is therefore  $\sqrt{B + L}/L$ . By extending the counting period this relative error can be made as small as desired, even when  $B/L$  is in the order of or exceeds unity (strong background, weak source of radiation). The weaker the background, however, the shorter the test period may be for a prescribed accuracy. For this reason a Geiger-Müller counter should have the least possible background.

The background is mainly due to the ever-present cosmic radiation, but it is often found to have a greater value than that calculated from the intensity of that radiation alone, and this difference cannot always be fully accounted for. The background can be reduced by making the counter volume smaller; for some measurements this may be an advantage, but for others not so, because then the number of radioactive particles picked up is also reduced. Further, the counter can be screened with a lead jacket, the specimen then being placed inside the jacket.

*Fig. 4* also shows that when the radiation is of great intensity the efficiency of the counter is reduced. This is due to the Geiger-Müller counter having a finite "dead time" and consequently a limited resolving power. By "dead time" is to be understood the interval of time elapsing between the beginning of a discharge and the moment when the counter tube is again able to respond to an incident particle. It comprises two parts, the dis-



*Fig. 4.* The number of counts per second ( $n$ ) produced by the tube, plotted as a function of the number of particles ( $p$ ) entering the counter per second, for the case of a beta counter with an efficiency of 100% for an average radiation intensity. For a low intensity radiation the background ( $a$ ) limits the accuracy of measurements. At very high intensities the resolving power of the counter sets a limit to the number of counts registered. This resolving power is determined by the finite dead time of the counter  $\tau$ ; when  $p$ , and thus  $n$ , becomes of the order of  $1/\tau$  the curve bends to the right.

<sup>2</sup>) See for these problems: J. Bleeksmas, G. Kloos and H. J. Di Giovanni, X-ray spectrometer with Geiger counter for measuring powder diffraction patterns, *Philips Techn. Rev.* **10**, 1-12, 1948.



charge time, i.e. the time during which the discharge is taking place, and the recovery time, i.e. the time it takes, after quenching of the discharge, for the slowly moving, positive, gas ions to reach the cathode. During the latter interval of time these gas ions so influence the field that the ionisation brought about by a new particle is unable to initiate a new discharge. The counter does not become sensitive again until the gas ions have approached to within a certain distance from the cathode, but the pulse that can be produced at that moment is smaller than before the discharge. When all the ions have reached the cathode the tube again functions normally. Both the discharge time and the recovery time depend upon the gas filling, the voltage applied and the dimensions of the counter, and the circuit employed (threshold value).

It will be clear that if the radiation is so intense that several particles occur in a period of time equal to or shorter than the dead time, then these particles will not each produce a pulse. Thus the efficiency of the counter is reduced when the average frequency of the particles becomes of the order of the reciprocal of the dead time. In other words, the finite resolving power of the counter tube sets an upper limit to the radiation intensities that can be measured<sup>3)</sup>.

From the foregoing it is obvious that the dead time should be kept as short as possible. For most counters it is in the order of one tenth of a millisecond.

### The gas filling of a Geiger-Müller counter

As already remarked, the composition and pressure of the gas in a Geiger-Müller counter should be so chosen that the self-sustained discharge following the entry of a particle is quickly quenched, be it with or without the aid of certain circuits.

#### Counters with statistical quenching

Originally, for the filling of a Geiger-Müller tube gases like hydrogen, nitrogen and air were used, possibly with a rare gas added<sup>4)</sup>.

In a counter tube filled with such a gas the ignition is followed by a stationary gas discharge. By employing a large load resistance for limiting the tube current to small values this discharge can be arranged to quench itself after a certain time. As

the current passing is very small, so few particles take part in the discharge that its statistical fluctuations are large enough to quench the discharge entirely (cf. fig. 5). This can be understood when we come to consider the mechanism by which the discharge is maintained under low pressures. On its way towards the anode an electron formed between the electrodes releases a number of ions and other electrons, the latter doing the same in turn. At the same time a number of radiation quanta

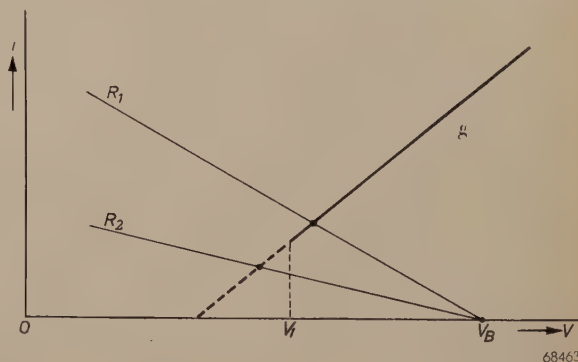


Fig. 5. The current  $i$  passing through a statistically quenching Geiger-Müller tube plotted against the tube voltage  $V$  (current-voltage characteristic, line  $g$ ). A load resistor is connected in series with the tube. With a given load resistor  $R$  the voltage at the tube during a discharge adjusts itself to the value corresponding to the point where the line  $g$  intersects the "resistance line" for the value  $R$ . The latter line intersects the abscissa at the point  $V_B$  corresponding to the supply voltage, the slope of the line being inversely proportional to the resistance. For a resistance ( $R_2$ ) exceeding a given value the point of intersection lies on the broken part of the characteristic (tube voltage  $< V_1$ ); the discharge is then unstable and is quickly quenched. For smaller resistances ( $R_1$ ) the discharge is stable.

are formed. If these ions and quanta release only just one electron from the cathode the discharge is maintained. If, however, the statistically fluctuating number of particles in one of these processes drops below a certain limit, the succession is interrupted and the discharge quenched.

In fact the duration of the discharge itself shows statistical fluctuations, an example of which is to be seen in fig. 6, representing the discharge current in an argon-hydrogen counter as a function of time and showing a number of successive discharges, about 100, traced on the screen of a cathode-ray oscilloscope and photographed. The fluctuations in the duration of the discharge are clearly seen. The two photographs, taken for average discharge currents differing by a factor of about 3, give an idea of the relation between the average duration of the discharge and the average current. This average value of the discharge time forms part of the dead time of the counter, and to keep it small it is necessary to make the current small and thus to give the load resistance a higher value, the latter being

<sup>3)</sup> With low radiation intensity, too, it may happen that one particle follows another in a period of time shorter than the dead time. In practice, however, the loss in efficiency with a low radiation intensity is mostly negligible.

<sup>4)</sup> See, e.g., A. Bouwers and F. A. Heyn, A simple apparatus for counting electrons, Philips Techn. Rev. 6, 75-79, 1941.



about  $10^{10}$  ohms. This, however, has the drawback that after the discharge has ceased the original voltage across the counter is but slowly restored, so that the recovery time, and thus the dead time, is again lengthened. This effect can be minimized by employing in the place of a simple resistor a valve circuit, whereby a series resistance of about  $10^6 \Omega$



Fig. 6. Current flowing through the tube as a function of time in the case of a statistically quenching counter filled with argon and hydrogen. The oscillogram shows about 100 superimposed sweeps. The discharge always begins at the peak. There are considerable statistical fluctuations in the duration of the discharge. The average duration of the discharge depends on the tube current. The current after the ignition amounts in (a) to  $0.12 \mu\text{A}$ , in (b) to  $0.35 \mu\text{A}$ . The supply voltage is 870 V; the total duration of the time base sweep is 1.75 msec.

can be used instead of  $10^9$  to  $10^{10} \Omega$  (e.g. a Neher-Harper or a Neher-Pickering circuit; see the article quoted in footnote 4)).

The counter tubes described above are occasionally called non-self-quenching counters, but in principle this is not the right name for them since in fact they are indeed self-quenching, though this takes place slowly and varies in duration. It is therefore better to speak of them as slow counters. The voltage range within which these counters operate extends from about 900 V to 1500 V. Examples are the Philips counters for gamma rays, types 18500 and 18501, made of stainless steel with a wall thickness of 0.3 mm and 0.1 mm respectively. The type 18501 can be used also for hard beta rays. The dead time of these counters (connected in their proper circuits) is about  $10^{-4}$  sec. They have an unlimited life and their background (without screening of the tube) is less than 20 counts per minute.

### Counters with space-charge quenching

Another type is the so-called self-quenching counter, which when used in series with a not very large load resistor is quenched spontaneously in a practically constant and relatively short time. These counters are also called rapid counters, which is a better name for them. They are characterized by certain admixtures in their gas filling.

In 1937 Trost discovered that an admixture of ethyl alcohol to the argon gas makes the counter tube self-quenching even if the load resistor has a low value. Other organic gases were also found to be useful as quenching gases, e.g. methane, amyl acetate, methylene bromide and tetramethyl lead.

The operating voltage of these counters lies at about 1000 V or higher, which is about the same as that of the slow counters, while their dead time is likewise about  $10^{-4}$  sec but there is no need to use special circuits.

It is generally assumed that in these counters, owing to the presence of the quenching agent, the density of ionisation produced is so great that after the electrons have disappeared from the tube (they travel to the anode wire very quickly) a large space charge of positive ions is left. The field strength near the anode thus drops quickly below the value required for further ionisation and the discharge is quenched. The discharge time is therefore short. As the ions move towards the cathode the field strength at the anode is restored and the counter gradually regains sensitivity for new particles.

If the ions were to release sufficient new particles from the cathode the tube could be re-ignited, but the presence of the quenching gas appears to prevent this. A great drawback attaching to these counters with organic admixtures in the gas filling is that they have a finite and rather short life and during their lifetime vary in sensitivity. Both these effects are due to dissociation of the organic molecules through collision with electrons or to the absorption of photons, since the effect of the fragments of the molecules upon the quenching and the position of the plateau of the counter is different from that of the original molecules. Furthermore, these phenomena may have an adverse effect upon the properties of the counter when they are deposited on the anode or the cathode. The temperature (vapour pressure of the quenching gas) also influences the operation of the tube, causing variations in the plateau and thus in the adjustment and efficiency of the counter. In the course of time a great variety of radicals appear in the tube, until decom-



position has progressed so far that too many substances with unfavourable properties (electron capture, pollution of electrode surfaces) are formed and render the counter unserviceable. The rate at which this takes place depends upon the nature of the quenching gas. With large organic molecules it takes longer than with small molecules, like those of ethyl alcohol, before the fragments formed are so small that quenching becomes ineffective. Further, the life of the counter is influenced by the circuit in which it is used: if the circuit is such as to accelerate the quenching then this gives the counter a longer life. It is therefore advisable to use a quenching circuit also with these rapid counters.

The life of an alcohol counter is in the order of  $10^7$  to  $10^9$  counts, whilst its background is in the order of 10 to 20 counts per minute, depending upon its construction.

### Halogen counters

In 1937 Geiger and Haxel (German patent 682 657) advised the use of halogens, in whole or in part, for the filling of counting tubes. These counters were claimed to be self-quenching and to have a long life. In the years that followed this idea was worked out further, mainly in the U.S.A.<sup>5)</sup>, with the result that now there are very useful self-quenching counters with unlimited life and a low operating voltage.

These so-called halogen counters contain a rare gas, or a mixture of rare gases, with a small quantity of an halogen added. The halogen, of which only chlorine and bromine need be considered (fluorine is too reactive, while the vapour pressure of iodine is too dependent upon temperature), acts as the quenching gas. Dissociation of the halogen molecules in such a tube does not permanently reduce the amount of quenching gas available, because after a time the fragments recombine into complete molecules. This accounts for the practically unlimited life and constancy of halogen counters.

Halogens have a greater destructive effect upon the materials of the tube than the organic gases, but this can be avoided by a suitable choice of materials. Many of the materials commonly used in the construction of counter tubes are, therefore, unsuitable for halogen counters.

As is the case with all self-quenching counters, the discharge time is, practically speaking, not subject to statistical fluctuations, nor is it greatly influenced by the current passing through the tube.

This is illustrated in *fig. 7*, which should be compared with *fig. 6*: a large number of discharges (about 100) have again been recorded on a photographic plate. It appears that, notwithstanding the greatly differing load resistances and voltages, there is practically no variation in the average discharge

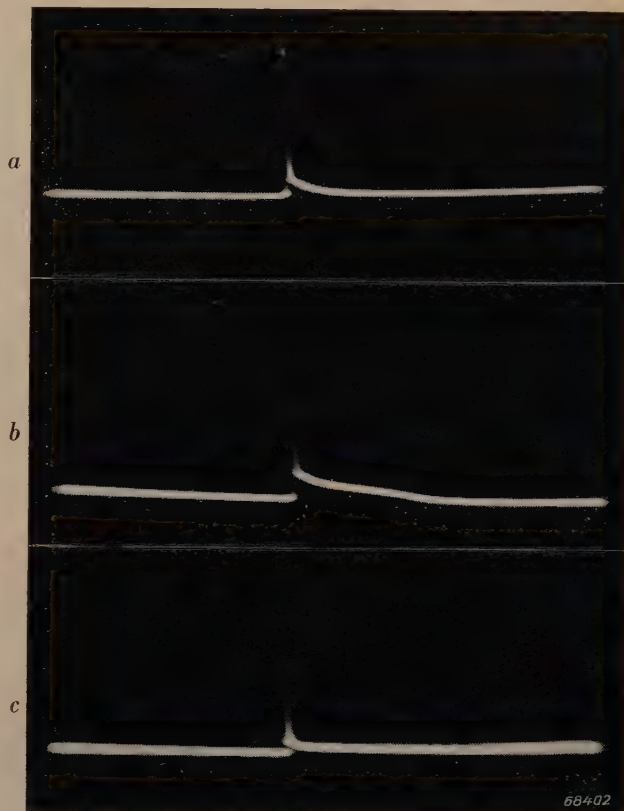


Fig. 7. As in *fig. 6* but for a space-charge quenched halogen counter. The load resistor for (a) is  $1000\text{ M}\Omega$ , for (b) and (c)  $10\text{ M}\Omega$ . The supply voltage for (a) and (b) is 350 V and for (c) 300 V. Here, again, about 100 counts have been registered in succession. There is no longer any question of statistical fluctuations in the duration of the discharge. The total duration of the time-base sweep is 0.62 msec.

time and that, likewise under these differing conditions, the individual pulses are equal in height. Even when the load resistance used is so small that there is a great tendency to form a continuous discharge (cf. *fig. 5*) the pulse is still of the same duration. Here there is no indication at all of a gradual transition from pulses of increasing duration to a continuous discharge, as is the case with statistically quenching counters, when the load resistance is reduced.

### Low-voltage counters

Until recently the voltage for a normal counter tube was in the order of 1000 V. In many cases a lower operating voltage would be preferable, namely where a battery is the source of supply. In some circuits it is also advantageous if the tube voltage

<sup>5)</sup> S. H. Liebson and H. Friedman, *Rev. Sci. Instr.* **19**, 303, 1948.; S. H. Liebson, *Rev. sci. Instr.* **20**, 483, 1949.



is no higher than the voltage on the electronic valves employed in the circuit. Of course the working voltage can be lowered somewhat by varying the pressure in the counter, but then the counter usually loses sensitivity.

The great influence of certain admixtures upon the disruptive voltage of a gas has been known for a long time <sup>6)</sup>. It appears that in general a lowering of the disruptive voltage may be expected if the gas atoms possess a metastable state where their excitation energy is higher than the ionisation energy of the admixtures. The metastable atoms are then able to return to a lower state by giving off their excitation energy to the foreign atoms, which are thereby ionised. Thus for the same tube voltage more ions are obtained than when there are no admixtures in the gas, and the disruptive voltage is lower. For instance, neon with 0.1% argon has a minimum disruption voltage of about 165 V — for plane parallel iron electrodes — whilst under the same conditions pure neon has a disruptive voltage of 450 V.

It might be thought that this mixture could be used to give a counter tube a low starting voltage for a self-sustained discharge. However, to prevent the positive argon or neon ions, and any remaining metastable neon atoms (which have a long life and are not influenced by the field), from causing re-ignition the potential must be lowered a long time after each count, which means that the counter is very slow in its action and a special quenching circuit is required. (Such a circuit has in fact been used by Simpson.) If, however, a little halogen is also added to the mixture to act as quenching agent, the counter quenches itself in a short space of time. With this extra admixture the disruptive voltage is slightly raised, but since the quantity of halogen needed for quenching is only very small it is possible to make in this way a self-quenching counter with a working voltage of 250 V at a normal gas pressure (about 10 cm mercury). The halogen molecules themselves can also serve as pick-ups for the meta-

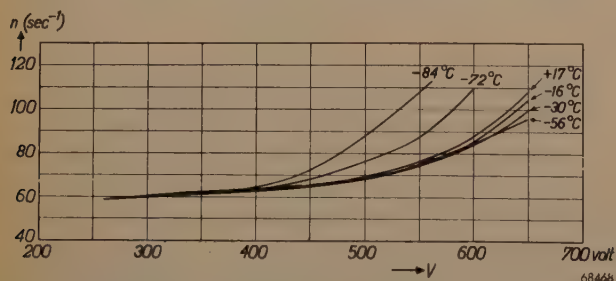


Fig. 8. Plateau of the counting characteristic of a low-voltage halogen counter at different temperatures.

<sup>6)</sup> See, e.g. M. J. Druyvesteyn and F. M. Penning, *Rev. mod. Phys.* **12**, 87-174, 1940.

stable excitation energy (neon-bromine mixtures), but then the disruptive voltage is often rather higher than when argon is also added to the gas filling.

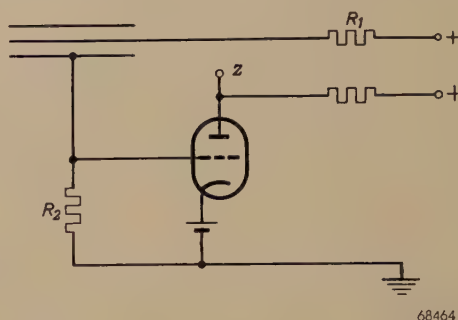


Fig. 9. Circuit with which the plateaus given in this article have been measured. The pulses are taken off at  $z$ .

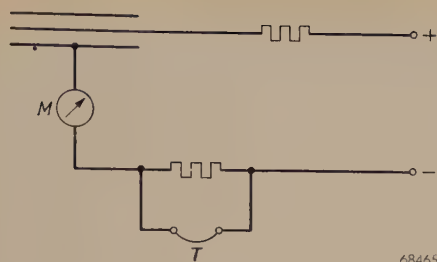
For some applications of low-voltage counters the counting characteristic has to be insensitive to relatively large temperature fluctuations. In *fig. 8* the plateau of the counting characteristic is shown for a low-voltage halogen counter, measured at different temperatures, in the simple circuit of *fig. 9*. From this diagram (*fig. 8*) it is seen that between about  $-60$  and  $+17$  °C the influence of temperature is negligible, the length of the plateau covering a range of 250 V and the slope being less than 5% per 100 V. The plateau likewise remains practically unchanged at higher temperatures up to 100 °C. The shortening of the plateau at temperatures below  $-70$  °C is due to condensation of bromine from the gas mixture.

Halogen low-voltage counters have a practically unlimited life, more than  $10^{11}$  counts having been reached in life tests. The background of low-voltage counters of about the same dimensions as the types 18500 and 18501 is about 25 counts per minute when they are not screened and 14 counts per minute when screened with a 5 cm layer of lead.

When halogen counters are used in one of the normal quenching circuits account has to be taken of the fact that sometimes the capacitance in parallel with the counter influences the quenching.

Counters with an organic gas as quenching agent can only withstand discharge currents of a few microamps, whereas halogen counters can be used in circuits where the current passing through the counter has a mean value of many microamps. (In fact halogen counters can withstand a glow discharge without any adverse effect, although the continuous currents occurring then are even higher.) Such a circuit is often employed in portable counting apparatus and is represented schematically in *fig. 10*. A direct-recording meter is used for high intensities and a head-phone for low intensities. Strong gamma or X-rays of some tens of Roentgen units per hour can quite easily be measured in this way. In such cases counters are often used whose sensitivity has been purposely reduced; see the last paragraph in this article.





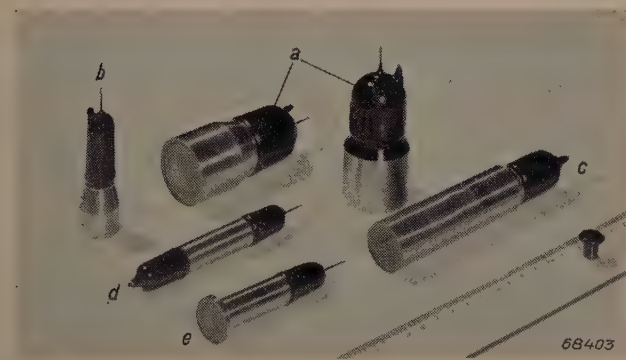
68465

Fig. 10. Simple measuring circuit using halogen counters. *M* microammeter, e.g. 0-25  $\mu$ A. *T* head-phone.

### Some particular types of counters

It has been shown that in the construction of Geiger-Müller counters for various purposes all sorts of problems are involved: the choice of materials for the tube and the anode wire, the composition and thickness of the window, the dimensions of the tube and the composition of the gas filling all have to satisfy different requirements for the various applications. Without going any further into these problems here, a summary is given, by way of illustration, of some prototypes of new counters designed by Philips.

Fig. 11 shows a number of halogen counters. The counter (*a*) for beta and gamma rays, operating at about 1000 V, with an inner diameter of 30 mm and a mica window of 10  $\mu$ , has a very long and flat plateau (length about 700 V, slope 3% per 100 V). Fig. 12 gives the counting characteristic of this tube measured in the simple circuit of fig. 9. The background amounts to 50 counts per minute (un-screened). A smaller type (*b*), diameter 15 mm and window 5  $\mu$  thick, is particularly suitable for measuring very soft beta rays and has a background of 18 to 20 counts/min. These two counters, designed for counting beta particles, also have an efficiency

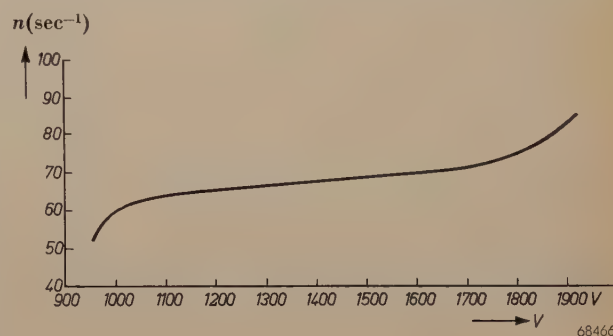


68403

Fig. 11. Some types of halogen counters: (*a*) Counter for beta and gamma rays, 30 mm internal diameter, with mica window 10  $\mu$  thick. (*b*) The same counter in a smaller size, internal diameter 15 mm, mica window 5  $\mu$  thick. (*c*) X-ray counter, int. dia. 19 mm, mica window 10-12.5  $\mu$ . (*d*) and (*e*) Low-voltage counters, for both beta and gamma rays, int. dia. 14 mm, those for gamma rays having a mica window (5 to 10  $\mu$  thick).

of about 2% for gamma rays. With a different gas filling they may also be given a working voltage of about 600 V, but the efficiency for gamma rays is somewhat reduced.

The tube (*c*) is intended for use in an X-ray diffraction apparatus<sup>2)</sup>. It is especially suitable for measuring the  $K\alpha$  radiation of copper, for which wavelength (about 1.5  $\text{\AA}$ ) the gas filling has good absorbing properties. The counter tube described in the article quoted in footnote<sup>2)</sup> contained methylene bromide as quenching agent. When this tube is replaced by the halogen counter (*c*) in fig. 11, with the same working voltage, which has in fact been done in a new model of the diffraction apparatus, a gain in sensitivity of 2.5 times is obtained. This is because the sensitive volume of the tube is confined to a volume around the anode wire, since many of the electrons formed are captured and lost in the rather



68466

Fig. 12 Plateau of the beta and gamma counter *a* in fig. 11. Slope 3% per 100 V, length about 700 V. The background of this counter screened with 5 cm lead amounts to 25 to 30 counts per minute.

large quantity of methylene bromide required in that tube for quenching. The very much smaller quantity of halogen required in the new tube intercepts so few electrons that practically the entire volume of the counter is sensitive. Furthermore, in the latter case the gas pressure can be slightly raised, which favours the absorption of the Roentgen quanta and thus also improves the efficiency of the tube. The plateau of this counter has a slope of 3% per 100 V and extends from 1300 V to beyond 2000 V (see fig. 13). The 12  $\mu$  mica window can, if desired, be replaced by a thinner one, down to 5  $\mu$ . The resultant gain in sensitivity is particularly important in measuring the softer chromium radiation. The background amounts to 50 counts per minute.

The tube (*d*) is a low-voltage counter for gamma rays and hard beta rays, while a similar tube (*e*) with mica window is intended for softer rays.

For some purposes it is advantageous to have an insensitive counter, for instance when a very high intensity of radiation is to be measured and the



resolving power of normal counters is exceeded. For hard gamma rays it is not at all convenient to render a counter insensitive by enveloping it in a lead jacket, and for portable counters it is quite impracticable. Two gamma-ray counters have therefore been developed like the type (d) in fig. 11; these are illustrated in fig. 14 side by side with the

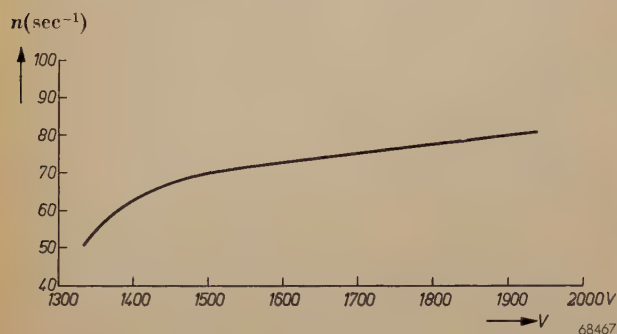


Fig. 13. Plateau of the X-rays counter *c* in fig. 11. This extends to beyond 2000 V and has a slope of about 3% per 100 V. The background is 50 counts per minute.

first type. One of these counters (*b*) is 20 times and the other (*c*) 200 times less sensitive than the original counter (*a*). They both operate at a relatively low voltage and have a small background corresponding to their dimensions.

**Summary.** The historical development of Geiger-Müller counters from the first original type up to the present-day designs is discussed with reference to the properties of gas

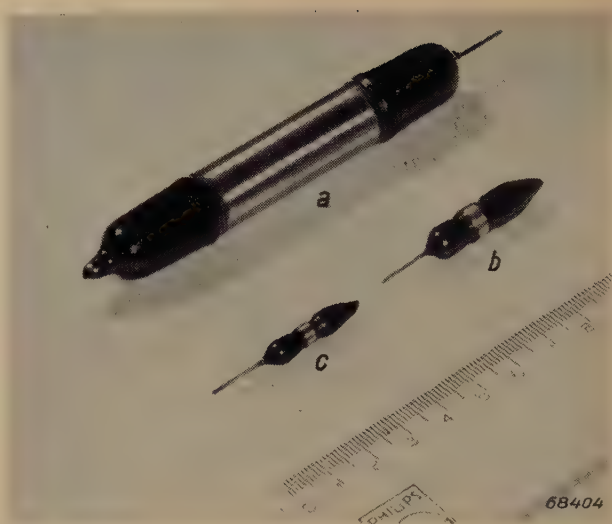


Fig. 14. Insensitive counters for gamma rays. (*a*) The same counter as *d* in fig. 11. (*b*) A counter 20 times less sensitive than *a*, (*c*) a counter 200 times less sensitive.

discharges, with a brief indication of the various ways in which a gas-discharge tube can be used for counting ionising particles or quanta. Particular consideration is given to the properties of counting tubes in the "Geiger-Müller range" (plateau) and the classification of existing counters into those with statistical quenching and those with space-charge quenching. The properties of the argon-hydrogen counter, an example of a statistically quenched tube, and those of the counter with an organic gas as quenching agent, an example of a counter with space-charge quenching, are gone into more closely. Finally the new self-quenching counters with halogen as quenching agent are described in various constructions and applications, mention being made, among others, of a low-voltage counter with a starting voltage of 250 volts, some types of beta and gamma counters with mica window, and a counter of great sensitivity for X-rays of about 1 to 2 Å wavelength; these counters have a practically unlimited life.



# THE STRUCTURE OF GLASS

by J. M. STEVELS.

666.1:539.213.1

---

*Although the material "glass" has now been known for some thousands of years, the variations in which it may be obtained are not by any means exhausted. This is evident from the fact that during the last decades many kinds of glass with new properties have been developed and found application in various technical directions. For the man of science it is gratifying to see that now, after centuries of empiric rule in this domain, in many cases theoretical conceptions as to the structure of glass are serving as a guide to the development of new materials.*

---

## Introduction

For many uses of glass, particularly in the field of electrotechnology, the requirements which have to be met nowadays go far beyond the properties that are usually to be found in normal kinds of glass. To illustrate this we have only to take a few cases occurring in the field of activity of our laboratories. For radar transmitting valves a glass is required which shows no excessive dielectric losses in an alternating field with frequencies in the order of  $10^{10}$  c/s (3-cm waves). For the transmitting valves used for normal radio broadcasting at frequencies round about  $10^6$  c/s (300 metres) the glass must likewise not have too high dielectric losses, whilst it must also have a low softening point for easy manufacture. The development of the cathode-ray tubes for television receivers particularly involves special glass-technical problems. For the small projection-television tubes, in which electrons are accelerated by voltages of 25 kilovolts or higher, a glass is required which is able to withstand lengthy bombardment by the electrons and by X-rays without being subject to discoloration.

It was fortunate that at the moment when such very special requirements as these were placed before the glass technologist some insight had already been obtained into the structure of glass in general. This suggested the lines on which further work could be done to reach the desired results.

The foundations for our present-day knowledge of the structure of glass were laid by Zachariasen<sup>1)</sup>, who in 1932 wrote a classical article on the subject. The theories he expounded have already been set forth in this journal<sup>2)</sup>, so that it will suffice to recall them here quite briefly. We shall then proceed to deal with the refinements which Zachariasen's theory has subsequently undergone on various points and

which are due mainly to the work of Warren and Weyl in the U.S.A. and of Dietzel and Smekal in Germany. It is due to these refinements in particular that we are not only able to grasp a number of peculiarities in the already known physical properties of glass but are now better prepared to cope with the new requirements of technical science.

## Zachariasen's theory

There are a number of oxides, called glass-forming oxides, which may occur in the vitreous as well as in the crystalline state ( $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ ). According to Zachariasen, in the crystalline and in the vitreous state these oxides are built up of the same elements, namely polyhedrons (tetrahedrons or triangles) of oxygen ions with the highly charged cations  $\text{Si}^{4+}$ ,  $\text{B}^{3+}$ ,  $\text{P}^{5+}$  at their centres. The only difference is that in the crystalline state these polyhedrons are arranged regularly, whereas in the vitreous state they are not. A schematic representation of this is given in *fig. 1*.

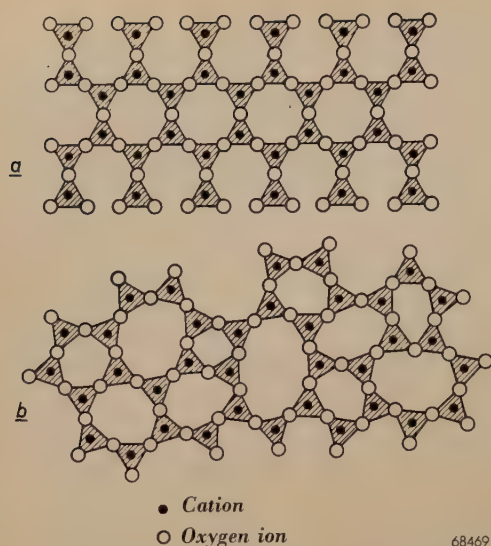
For the network of oxygen polyhedrons to occur in these two forms it is necessary that the structure of the oxide in the crystalline state satisfies a number of conditions given by Zachariasen, which (see the article quoted in footnote<sup>2)</sup>) involve the following.

1. Every oxygen ion must be bound to not more than two positive ions which must be highly charged and small.
2. The number of oxygen ions which surround such a positive ion (forming a polyhedron) must be neither very large nor small (3 or 4).
3. The oxygen polyhedrons adjacent to each other must have common corners (bridging oxygen ions), but no common edges or faces.
4. Each polyhedron must have at least three oxygen ions in common with neighbouring polyhedrons.

<sup>1)</sup> W. H. Zachariasen, J. Amer. Chem. Soc. **54**, 3841, 1932.

<sup>2)</sup> J. M. Stevels, Philips Techn. Rev. **8**, 231—237, 1946.





68469

Fig. 1. Two-dimensional representation a) of a crystalline lattice  $A_2O_3$  (A is a cation) and b) the corresponding network in the vitreous state.

We shall not enter into the arguments on which these rules have been formulated. Suffice it to say that oxides which in the crystalline state satisfy these conditions have a very open structure, so that the polyhedrons need not necessarily arrange themselves according to a periodic pattern when, upon cooling of the melt, the solid phase is formed.

The structure of the many glasses that can be made by fusing these glass-forming oxides together with a large number of metallic oxides, such as CaO, BaO, PbO, Na<sub>2</sub>O, is likewise described by the theory of Zachariasen. While the metal ions find a place in the interstices of the open network just mentioned, the added oxygen ions are taken up through a number of oxygen bridges in the network being broken, each bridging oxygen ion being replaced by two non-bridging oxygen ions. Obviously any continued change of this nature will greatly influence the properties of the glass.

Fig. 2. is a diagrammatic representation of the structure of such a glass.

Actually, of course, it is not each metal ion that seeks a place in an interstice of the network. It is better to say that while the melt is solidifying the oxygen chains arrange themselves around the metal ions. The presence of these ions modifies to some extent the form that the network finally assumes, and for that reason they have been given the name of network modifiers. The ions occurring in the centres of the oxygen polyhedrons, and which, therefore, together with the oxygen ions actually form the network, are called network formers.

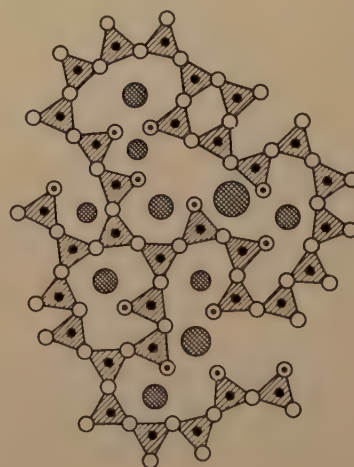
This simple theory of the structure of glasses

was verified about 1938 with the aid of X-ray diffraction photographs, mainly by Warren and his associates<sup>3</sup>).

We shall now proceed to discuss some of the aforementioned refinements of the theory that have been made in the course of the last ten years.

### The structure of borate glasses

It will be obvious that the addition of metallic oxides to a glass-forming oxide cannot be continued at will. It has already been pointed out that the breaking down of oxygen bridges greatly influences the properties of a glass, and one can imagine that if this is carried too far the typical vitreous structure of coherent tetrahedrons or triangles ultimately becomes unstable. It can readily be understood that a network completely spatially bonded is no longer possible as soon as the number of contact points (bridging oxygen ions) per polyhedron, denoted by  $Y$ , becomes less than two<sup>4</sup>). "Islands" are then formed, which in themselves may consist of a rather large number of polyhedrons. The smaller the value of  $Y$ , the smaller are the islands. For  $Y = 1$  these islands average two polyhedrons, whilst for  $Y = 0$  the "structure"



- Network-forming ion
- ⊙ Network-modifying ion
- Bridging oxygen ion
- ⊖ Non-bridging oxygen ion

68470

Fig. 2. Two-dimensional representation of the network of a glass containing, in addition to oxygen ions, both network-forming and various network-modifying ions. Non-bridging oxygen ions occur.

<sup>3</sup>) B. E. Warren and J. Bischoe, J. Amer. Ceram. Soc. **18**, 49, 1935; J. Bischoe and B. E. Warren, J. Amer. Ceram. Soc. **21**, 287, 1938.

<sup>4</sup>) J. M. Stevels, J. Soc. Glass Techn. **30**, 31, 1946; Ned. T. Natuurkunde **12**, 257, 1946.



consists of isolated polyhedrons. Obviously the structures with small  $Y$  values will have a strong tendency to order themselves, thus readily changing into the crystalline state.

The number of contact points per polyhedron,  $Y$ , can quite easily be calculated from the composition of the glass. In this connection the composition is characterized by the ratio  $R$  of the total number of oxygen ions to the total number of network-forming ions. For glasses with tetrahedrons as elements, i.e. with network-forming ions having a coordination number of 4 (silicate and phosphate glasses), the relation is <sup>5)</sup>:

$$Y = 8 - 2R, \quad . . . . . (1)$$

whilst for glasses with triangles as elements, i.e. with network-forming ions having a coordination of 3, the rule is:

$$Y = 6 - 2R . . . . . (2)$$

Silicate glasses can, indeed, only be formed as long as  $R \leq 3$ ; in other words, as soon as  $Y < 2$  (i.e. as soon as islands begin to form) it is no longer possible for the melt to solidify in the vitreous state. With phosphate glasses it appears that one can go a little farther in adding metallic oxides, as far as  $R = 3.2$ . Then  $Y = 1.6$ , which means that it is possible to reach the vitreous state notwithstanding the occurrence of (not too small) islands.

With borate glasses, considering that the  $B_2O_3$  structure consists of triangles, one would expect the addition of metallic oxides to cause formation of islands ( $Y < 2$ ) as soon as  $R > 2$ . With borium-containing glasses, however, a peculiar complication arises, in that in such glasses metallic oxides may be taken up according to a mechanism differing somewhat from that described above. When metallic oxides are added to  $B_2O_3$  — for instance  $Na_2O$  — the  $Na^+$  ions will find a place as network modifiers but the mechanism of bridge breaking does not take place. The excess of added oxygen is taken up owing to the property of the  $B^{3+}$  ion being able to occur in the centre of an oxygen triangle but also in the centre of an oxygen tetrahedron. Thus the network is then built up from both oxygen triangles and oxygen tetrahedrons, while there is not a single non-bridging oxygen ion. Such a structure is represented in fig. 3.

It is remarkable that this process of taking up oxygen, whereby a change takes place in the coordination number for some of the  $B^{3+}$  ions and the network gains more and more in strength, continues until a certain concentration is reached, which, for the system  $Na_2O-B_2O_3$ , is 18 mol. %  $Na_2O$ . With greater concentrations of  $Na_2O$  the previously described bridge-breaking mechanism comes into action again, non-bridging oxygen ions then being formed. These ranges of concentrations have been named respectively the accumulation region and the destruction region.

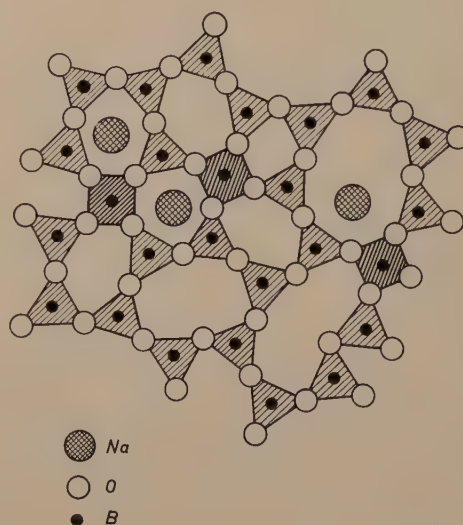


Fig. 3. Two-dimensional representation of a borate glass with small  $Na_2O$  content. This is characterized by the absence of non-bridging oxygen ions. ( $B^{3+}$  ions intriangular or tetrahedral surroundings are represented in the diagram by a coordination of 3 and 4 respectively in the plane of the drawing.)

The state of affairs outlined here implies that in such a borate glass relatively more metallic oxides can be taken up before island formation arises. In the accumulation region, where no non-bridging oxygen ions occur,  $Y$  always equals  $2R$  (cf. footnote <sup>5)</sup>), so that the average number of contact points per polyhedron increases with increasing  $R$ ! In the destruction region the ratio of the number of triangles to the number of tetrahedrons remains constant, such that the average coordination number of the  $B^{3+}$  ion  $Z = 3.22$ . In this region, therefore, the relation (cf. footnote <sup>5)</sup>) is:

$$Y = 6.44 - 2R . . . . . (3)$$

Island-forming ( $Y < 2$ ) will then not take place until  $R > 2.22$ . Actually it appears that most borates may become vitreous up to  $R = 2.4$ , so that here again, just as in the case of phosphate

<sup>5)</sup> Denoting the average number of non-bridging oxygen ions per polyhedron by  $X$  and the total number of oxygen ions per polyhedron (the coordination number) by  $Z$ , then, as may be verified by simply counting the ions,  $X + Y = Z$  and  $X + \frac{1}{2}Y = R$ , from which it follows that  $Y = 2Z - 2R$ .



glasses, a small degree of island-formation is no hindrance to vitrification.

The foregoing is illustrated graphically in fig. 4.

Of particular importance in practice are the consequences that the changing of the coordination number and the accompanying strengthening of the network have for the physical properties of this group of glasses. By way of example, in fig. 5 the coefficient of thermal expansion of the pure sodium-borate glasses is plotted as a function

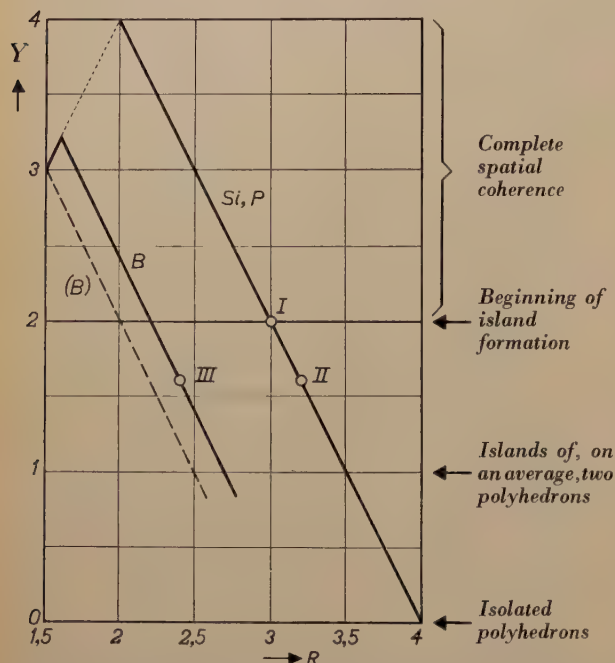


Fig. 4. Relation between  $Y$ , the average number of bridging oxygen ions per polyhedron, and  $R$ , the total number of oxygen ions divided by the total number of network-forming ions. The more metallic oxides are added to the glass-forming oxide, the greater is the value of  $R$ . The line  $Si, P$  applies for a network of tetrahedrons (eq. 1), the broken line  $(B)$  for a network of triangles (eq. 2).

From  $Y = 2$  onwards island-formation occurs. In the case of silicate glasses this indicates the limit to which  $R$  can be raised without devitrification occurring (point I). In phosphate glasses the vitreous state is still tenable up to  $Y = 1.6$ , i.e.  $R = 3.2$  (point II).

In the case of borate glasses the addition of metallic oxide is at first accompanied by a transition of  $B^{3+}$  ions from the coordination number 3 to the number 4; then  $Y = 2R$  (beginning of the sharply bent, fully-drawn line  $B$ ). When the coordination number has reached the average value  $Z = 3.22$  it remains constant and  $Y$  drops with increasing  $R$  according to eq. (3). Island formation ( $Y = 2$ ) then begins at  $R = 2.22$ , but for most borate glasses the vitreous state appears to be still possible up to  $R = 2.4$  (point III).

of their composition. This curve shows a minimum just at that composition where, according to the foregoing considerations, the network has the strongest structure.

Something similar is found in the case of borosilicate glasses. On the boundary line between the accumulation region and the destruction region (fig. 6) are the glasses which, compared with other

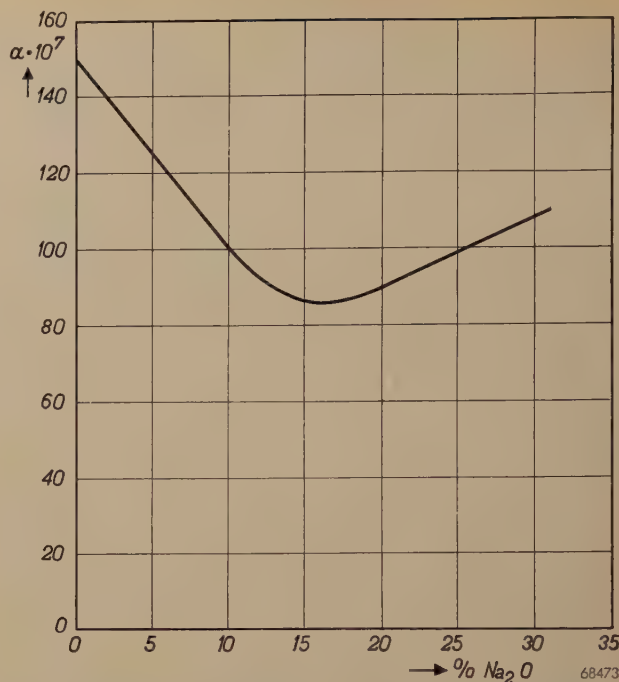


Fig. 5. The expansion coefficient of pure sodium-borate glasses as a function of the  $Na_2O$  content, expressed in weight %.

borosilicate glasses, are characterized by a maximum strength of structure (small expansion coefficient and high softening point), for example the "Pyrex" glasses.

The changing of the coordination number of the  $B^{3+}$  ion is therefore responsible for the fact that, under suitably chosen conditions, the incorporation in glass of  $B_2O_3$ , which itself has a very high expansion coefficient and very readily melts, results in a reduction of the expansion coefficient and a raising of the softening point. Various other

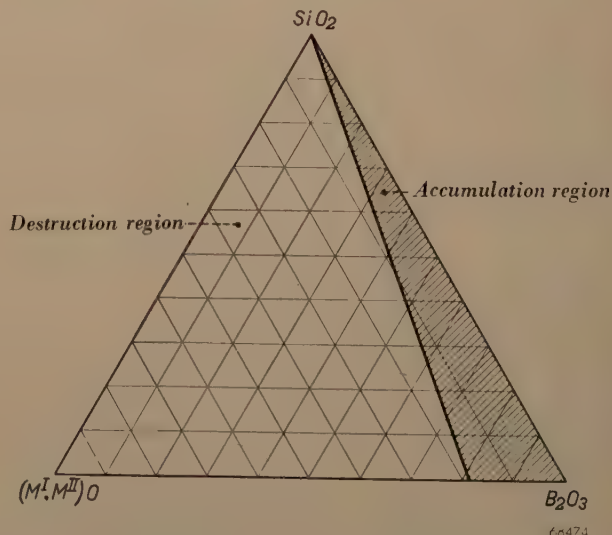


Fig. 6. Phase diagram of the system  $(M^I M^{II})O-B_2O_3-SiO_2$ , where  $M^I$  and  $M^{II}$  represent respectively a monovalent and a bivalent metal, which may occur in any proportions. The diagram can be divided into an accumulation region and a destruction region.



properties of the glass are likewise influenced by the structural change described, as for instance the dielectric losses. This will be discussed in greater detail in another article to be published shortly in this journal.

The conceptions of network-forming and network-modifying ions

Zachariasen thought that the positive ions could be divided into two groups, which in the foregoing have been denoted as network formers and network modifiers, but it has meanwhile become apparent that this division does not hold in all cases. It is now known that there are a large number of ions which may occur in glass in both forms, and often simultaneously. This means that in glass there are some ions of a certain type which have 4 oxygen ions surrounding them, thus being situated in the centre of the tetrahedrons forming the network typical for glass, while other ions of that type are surrounded by a larger number of oxygen ions. In some cases the position of the “equilibrium” between the two forms may be roughly determined by the colour of the glass, as is the case, for instance, with the nickel ion.  $\text{Ni}^{2+}$  ions may occur in a glass mainly as network formers, in which case the glass has a purple colour; under other circumstances these  $\text{Ni}^{2+}$  ions mainly occur as network modifiers, the glass then being yellow. Such differences in colour in cases where the coordination number is changed have been found, for example, with  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$  and  $\text{U}^{6+}$ . But it is also possible to detect these changes in the coordination number among non-colouring ions, by a method which has recently been indicated<sup>6)</sup> and which will be discussed in our next article.

The “equilibrium” between the forms of coordination depends not only upon a number of external factors (temperature and furnace atmosphere when making the glass, and the rate of cooling) but also to a large extent upon the quantities of the different ions contained in the glass. The simple theory of Zachariasen could not furnish any explanation for this, but it has been made comprehensible by means of a “competition principle”. In general, the small, highly charged ions which are capable of attracting the oxygen ions close to them, and strongly binding them, will easily surround themselves with only four oxygen ions (or three in the case of  $\text{B}^{3+}$ ). The larger and less charged cations are then surrounded by a larger number of oxygen ions, to

which they are less strongly bound. In principle, however, also these latter cations may be surrounded by only four oxygen ions, thus entering into competition with the small, highly charged ions, in which they may be successful, for instance, when relatively few oxygen ions are present.

Various investigators have attempted to express this “competition capacity” of the ions numerically. A suitable measure has been found to be the “field strength” of the ion at the centre of an adjacent oxygen ion,  $z/a^2$ , where  $z$  is the charge of the ion and  $a$  the distance between the centres of the two adjacent ions<sup>7)</sup>. When the ions are arranged in the order of their calculated field strength (see table I) their sequence gives an idea of the preference that the various ions have for occurring either as network formers or as network modifiers. When different cations occur in a glass simultaneously, those with the highest  $z/a^2$  value will preferably occupy the network-forming positions (smallest coordination numbers), while those with the lowest  $z/a^2$  value show a preference for the network-modifying positions (largest coordination numbers).

Table I. The “field strength”  $z/a^2$  for a number of cations, according to Dietzel<sup>7)</sup>;  $z$  = charge of the ion, expressed in elementary charges;  $a$  = distance (in Ångström) from the centre of the ion to the centre of an adjacent oxygen ion. (If the cation is rather large it then no longer fits in the interstice of a tetrahedron formed by four oxygen ions, and for this reason alone the natural coordination number is greater than four).

Coordination number Ion	3	4	6	8
$\text{P}^{5+}$	1.65	2.08		
$\text{B}^{3+}$		1.45		
$\text{Si}^{4+}$		1.57		
$\text{Al}^{3+}$		0.97	0.84	
$\text{Zr}^{4+}$				0.78
$\text{Be}^{2+}$		0.87		
$\text{Ni}^{2+}$		0.61	0.55	
$\text{Zn}^{2+}$		0.59	0.53	
$\text{Mg}^{2+}$		0.51	0.45	
$\text{Ca}^{2+}$			0.35	0.33
$\text{Ba}^{2+}$				0.24
$\text{Li}^{+}$			0.23	
$\text{Na}^{+}$			0.19	0.17
$\text{K}^{+}$				0.13

Some striking examples can be given to illustrate this.

When silicon ions and phosphor ions enter into competition with each other, as in the glass of the composition  $\text{SiP}_2\text{O}_7$  (i.e.  $\text{SiO}_2\cdot\text{P}_2\text{O}_5$ ), from the table

6) J. M. Stevels, Verres et Réfractaires 2, 2, 1948.

7) A. Dietzel, Glastechn. Ber. 22, 41, 1948.



it is to be predicted that the phosphor ions will "win". For this glass it is difficult to determine directly with what coordination numbers the ions  $\text{Si}^{4+}$  and  $\text{P}^{5+}$  occur in it. The crystalline  $\text{SiP}_2\text{O}_7$  has never been examined in this respect either, but crystalline  $\text{ZrP}_2\text{O}_7$ , which is isomorphous, as. By X-ray diffraction analysis it was found that each  $\text{P}^{5+}$  ion is indeed surrounded by four bridging oxygen ions and each  $\text{Zr}^{4+}$  ion by six bridging oxygen ions. Since it may be assumed that the coordination numbers will be the same in the vitreous state and in the crystalline state, we have here a case where  $\text{Si}^{4+}$  occurs in a coordination of 6, i.e. the  $\text{Si}^{4+}$  ion, the network former *par excellence*, occupies only a network-modifying position.

The opposite effect is seen in the following example. Of the compound  $2\text{CaO} \cdot \text{SiO}_2$  only a crystalline form is known. This is in conformity with the aforementioned considerations about  $Y$  and  $R$ : for four oxygen ions there is only one network-forming ion, thus  $R = 4$  and therefore, according to eq. (1),  $Y = 0$ . Though this substance is built up from  $\text{SiO}_4$  tetrahedrons, these are all isolated and therefore arrange themselves into a well-ordered structure, with  $\text{Ca}^{2+}$  ions as "binder". The remarkable fact is that the entirely analogous compound  $2\text{ZnO} \cdot \text{SiO}_2$  may indeed occur in the vitreous state. An explanation for this may find support in the fact that  $\text{Zn}^{2+}$  stands some steps higher in table I than  $\text{Ca}^{2+}$ . It is therefore feasible that in the system in question  $\text{Ca}^{2+}$  occurs exclusively with a coordination number six or higher, i.e. as a network modifier, whereas under suitably chosen conditions  $\text{Zn}^{2+}$  may occur also with coordination number four, thus possibly playing the part of a network-forming ion. If in the compound  $2\text{ZnO} \cdot \text{SiO}_2$  only 16.7% of the  $\text{Zn}^{2+}$  ions occur as network formers — instead of writing  $\text{Zn}_2\text{SiO}_4$  the composition can then be better written as  $\text{Zn}_{5/3}(\text{Zn}_{1/3}\text{Si})\text{O}_4$  — then the quotient  $R$  is already reduced to exactly 3 and thus vitrification is possible ( $Y = 2$ ). Actually slightly more than 16.7% of the  $\text{Zn}^{2+}$  ions will be present as network formers. Vitrification in the system  $\text{ZnO} \cdot \text{SiO}_2$  continues until roughly the composition  $2.2 \text{ZnO} \cdot \text{SiO}_2$  is reached. The condition  $R \leq 3$  can then only be satisfied if at least 18.2% of the  $\text{Zn}^{2+}$  ions occupy a network-forming position <sup>8)</sup>.

<sup>8)</sup> Here it is tacitly assumed that the limit found in practice for the occurrence of the vitreous silicates ( $R=3$ ) would likewise apply for the glasses containing  $\text{Si}^{4+}$  and few  $\text{Zn}^{2+}$  ions as network formers. *A priori* this need not strictly be the case, it being possible for the limit to lie at a somewhat greater value of  $R$  ( $Y < 2$ ) (cf. the phosphate and borate glasses). Then smaller percentages of network-forming  $\text{Zn}^{2+}$  ions would be sufficient to account for vitrification in the case of the compositions mentioned.

Certain barium-containing silicate glasses (the heavy barium crown glasses) have been shown to contain a number of barium ions forming part of a typically tetrahedral formation. Thus even  $\text{Ba}^{2+}$  ions may sometime play the part of network formers.

Resuming, the following advances have thus been made upon the old theory. According to Zachariasen's criteria  $\text{Zn}^{2+}$  and  $\text{Ba}^{2+}$  ions should always behave as network modifiers. The new conception (the competition principle) makes it feasible that such ions may also occur as network formers, and that such is more likely to be the case the greater the concentrations in which these ions are present. This is of great practical importance, since the addition of one and the same ion to a glass may influence the properties to a different extent (or even in the opposite direction), depending upon the position it takes in the network: the  $\text{Mg}^{2+}$  ion, for instance, yields, as network modifier, a contribution towards the dielectric losses of a glass at  $10^6$  c/s, whereas as a network former it is harmless in this frequency range.

#### How the nature of the bond influences vitrification

The theory of Zachariasen has undergone a considerable evolution in recent years in yet another respect. Whereas Zachariasen never discussed the nature of the bond in vitreous systems and, moreover, regarded the elements (the polyhedrons) as being invariable, in recent years it has been pointed out, especially by German investigators, that the nature of the chemical bond in the elements is of great importance in determining whether a certain substance may or may not occur in the vitreous state. Smekal, to whose work this theory is mainly to be ascribed, has indicated that it is feasible <sup>9)</sup> that a condition for vitrification is that the system must contain "mixed" bonds. By this it is meant that, in addition to directed bonding forces (homopolar bonds, which are confined to certain mutual "valence angles", such as, e.g., in  $\text{CO}_2$  or  $\text{NH}_3$  or  $\text{SiCl}_4$ ), also non-directed bonding forces (heteropolar bond or Van der Waals bond) must be in action. The two kinds of bonding forces may be united in one bonding direction, such as, e.g., in the Si-O bond, which is to be described as a combination of a force of the type of a homopolar bond and one of the type of a heteropolar bond, or they may be present in different bonding directions. The latter is found to be the case, for instance, in the vitreous selenium and in

<sup>9)</sup> A. Smekal, Nova Acta Leopoldina **11**, 511, 1942; worked out in more detail in Glastechn. Ber. **22**, 278, 1949.



the chain macromolecules, where in the direction of the chains a homopolar bond prevails while the chains are mutually kept together mainly by a Van der Waals bond<sup>10</sup>).

These considerations are of great importance because they relate to all kinds of glasses, whereas Zachariasen's theories apply exclusively to kinds of glass formed by inorganic oxides.

The difference between Smekal's theory and that of Zachariasen may be formulated by saying that the latter theory ascribes the irregular structure of the network exclusively to the irregular packing of the oxygen polyhedrons. According to Smekal's theory, applied to the oxide glasses, the type of bond within the polyhedrons may change, in that the bond may bear a more homopolar or a more heteropolar character. Consequently, therefore, interatomic distances in those polyhedrons may change, and this may also contribute towards the irregular structure of the network in vitreous systems.

#### Inorganic glasses in which Zachariasen's rules do not hold

Having accepted this line of thought as being correct, one will not be surprised to find that inorganic systems exist which do not at all obey the rules given by Zachariasen and nevertheless occur in the vitreous state.

Excluding those resembling selenium (such as vitreous sulphur and tellurium), the earliest known example is the system of carbonates  $K_2CO_3$ - $MgCO_3$ . According to Zachariasen's rules, as applied to the oxide  $CO_2$ , there would be no question of vitrification here; one would rather expect a regular crystal lattice formed by the positive metal ions and negatively charged  $CO_3^{2-}$  groups. It has now been found, however, that the heating of a mixture of  $K_2CO_3$  and  $MgCO_3$  in equimolecular quantities does indeed lead to vitrification. The glass certainly has a strong devitrifying tendency: at 300 °C it completely devitrifies in an hour, but at temperatures below 150 °C the vitreous state is maintained. Quite analogous systems, such as  $Na_2Ca(CO_3)_2$ ,  $K_2Ca(CO_3)_2$ ,  $Na_2Mg(CO_3)_2$ ,  $NaLiCO_3$  and  $KLiCO_3$ , on the other hand, show no trace of vitrification.

Looking back at table I, it is seen that of all the cations in question here  $K^+$  and  $Mg^{2+}$  differ most in "field strength". The fact that of the systems mentioned only  $K_2Mg(CO_3)_2$  forms a glass is an indica-

tion that the condition favourable for vitrification is created by the combination of a very weak and a much stronger cation. It may, therefore, be so interpreted that the greatly varying electric fields prevailing in the system deform the  $CO_3^{2-}$  groups in a different way, thereby, according to Smekal, promoting vitrification.

Something similar has been found with the nitrates. A mixture of equimolecular quantities of  $Ca(NO_3)_2$  and  $KNO_3$  becomes vitreous when cooled from the molten state, whereas such is not the case with the system  $Ca(NO_3)_2$ - $NaNO_3$ . Apparently the difference in strength of the  $Ca^{2+}$  ion and the  $Na^+$  ion is not large enough for a sufficient deformation of the  $NO_3^-$  groups. On the other hand the system  $Mg(NO_3)_2$ - $KNO_3$  would, indeed, be expected to occur in the vitreous state, and this has in fact been found to be the case. This is not so easily proved because it is difficult to obtain anhydrous  $Mg(NO_3)_2$  in a chemically pure state. In the procedure followed by us a mixture of  $Mg(NO_3)_2 \cdot 4H_2O$  was melted in a platinum crucible (the melting point is 92 °C) and then carefully heated further, thereby removing all the water contained in it. As soon as the melt begins to give off nitrous vapour (at about 290 °C) an equimolecular quantity of  $KNO_3$  is added. The homogeneous melt of  $KMg(NO_3)_2$  thereby obtained is quenched by decanting in droplets in liquid air. X-ray diffraction photographs showed that the product was vitreous.

With the sulphates there is a still more striking example. The system  $K_2SO_4$ - $MgSO_4$  does not, in any composition, yield a vitreous product, notwithstanding the great difference in strength between the  $K^+$  and the  $Mg^{2+}$  ions. When, however, the  $Mg^{2+}$  ion is replaced by an ion with a still stronger field, viz. the  $H^+$  ion, vitrification is possible: by heating  $KHSO_4$  to just above the melting point and then quenching by decanting onto an iron plate, a glass is obtained. At a temperature of 70 °C this glass can be drawn into threads.

Finally, a very striking confirmation of Smekal's theory has been found with normal oxide glasses themselves<sup>11</sup>). According to what has been set forth above, in a system such as, for instance,  $Na_2O$ - $B_2O_3$  vitrification occurs as long as the amount of  $Na_2O$  does not exceed a certain percentage corresponding to a value of  $R \approx 2.4$ . The same limit is found for the system  $K_2O$ - $B_2O_3$ . When examining, however, the mixed alkali borates, such as the system  $Na_2O$ - $K_2O$ - $B_2O_3$ , it is found that there are kinds of glass where  $R$  is much greater

<sup>10</sup>) In the light of these considerations it will be realized that theoretically it is difficult to find justification for the classification of the ions according to Dietzel's criterion, which is based entirely upon a heteropolar bond picture. Nevertheless it has been found very useful as a heuristic and didactic principle.

<sup>11</sup>) A. W. Bastress, *Glass Science Bull.* 4, 133, 1946; 6, 9, 1947; 6, 12, 1947.



than the limit mentioned. The same phenomenon is found with the mixed alkali silicates and alkali phosphates, such as illustrated for some systems by the phase diagrams in *figs 7 and 8*. As far as the value of  $R$  is concerned, the area of vitrification would be expected to be bounded in each diagram by the broken line: as a matter of fact vitrification

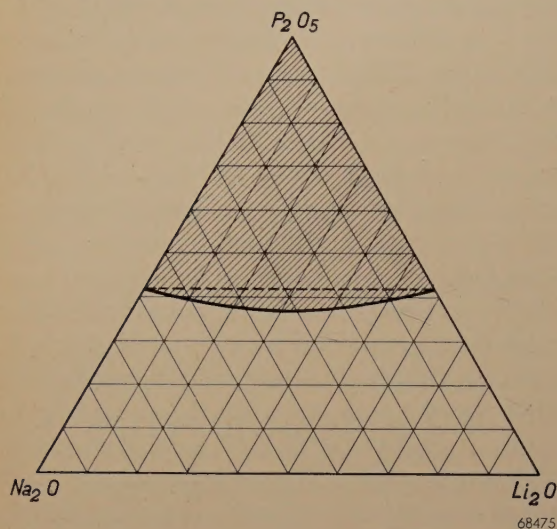


Fig. 7. Phase diagram of the system  $\text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{P}_2\text{O}_5$ . The vitreous state may be obtained with any composition in the hatched area. (Figs 7 and 8 have been taken from the publications by Bastress quoted in footnote <sup>11</sup>.)

occurs within the whole of the hatched area. The most striking fact is that the relative increase of the vitrification area is on the whole larger the more the respective cations differ in „field strength”;

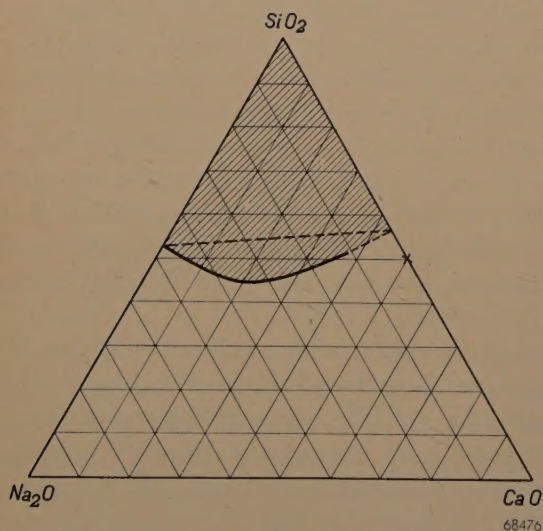


Fig. 8. Phase diagram of the system  $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ . The vitreous state may be obtained with any composition in the hatched area. Contrary to this diagram, according to J. B. Ferguson and H. E. Merwin (Amer. J. Sci. **48**, 81, 1919) a substance of the composition  $\text{CaO}.\text{SiO}_2$  (denoted by a cross in the diagram) can occur in the vitreous state; thus here  $R = 3$ .

for an example see *table II*. Herein lies the explanation for the whole phenomenon. The threshold value of  $R$  is related to the fact that with increasing number of oxygen ions the polyhedrons, originally considered as being entirely rigid, are ultimately no longer able to retain their mutual coherence in a network that is becoming more and more open. Owing to the great variations in the electric fields, however, the oxygen polyhedrons are themselves somewhat deformed. This deformation makes it possible for a coherent vitreous network to be formed also when the value of  $R$  is somewhat greater (smaller  $Y$ ).

Table II. Relative expansion of the vitrification area in the phase diagram of mixed alkali borates, compared with the area in which the condition for  $R$  is satisfied <sup>11</sup>).

System	Increase in %
$\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{B}_2\text{O}_3$	15
$\text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{B}_2\text{O}_3$	50
$\text{Li}_2\text{O}-\text{K}_2\text{O}-\text{B}_2\text{O}_3$	100

In conclusion it may be said that due to recent refinements of Zachariasen's theory many details in the phenomenon of vitrification can now be better understood. In particular the existence of all sorts of glasses not fitting in the old scheme has become understandable, while the new conceptions may serve as a guide — and in many cases have already so served — when seeking new glasses possessing entirely new combinations of properties.

**Summary.** Zachariasen's theory indicates under what conditions oxides may occur in the vitreous state. These conditions are based upon a conception of the structure of glass as an irregular network of oxygen tetrahedrons (or triangles) in whose centres are situated the small, highly charged ions  $\text{B}^{3+}$ ,  $\text{Si}^{4+}$  or  $\text{P}^{5+}$  (network formers), while in the interstices of the network there may be taken up, as network modifiers, all sorts of large, less charged, cations surrounded by a larger number of oxygen ions. According to new conceptions this picture has to be refined in some respects. The coordination numbers are not fixed to the extent originally supposed. The number of oxygen ions surrounding  $\text{B}^{3+}$  may change from 3 to 4, thereby explaining various phenomena encountered with borate glasses. Further, under certain conditions typical network modifiers (with normal surroundings of, say, 6 or 8 oxygen ions) may act as network formers (with coordination number four), and vice versa. The behaviour of the cations in this respect is governed by a competition principle, to which expression is given by a classification according to the order of their „field strength”. According to Smekal the occurrence of bonding forces of different types between the particles in the network is essential for vitrification. Many facts not covered by Zachariasen's theory, or in contradiction therewith, thus find a plausible explanation. A number of examples are given by way of illustration.